PB86-172095

Preliminary Assessment of Hazardous Waste Pretreatment as an Air Pollution Control Control Technique

Research Triangle Inst.
Research Triangle Park, NC

Prepared for

Environmental Protection Agency, Cincinnati, OH

Mar 86

U.S. Department of Commerce
National Technical Information Service
NTIS

EPA/600/2-86/028
March 1986

PB86-172095

PRELIMINARY ASSESSMENT OF HAZARDOUS WASTE PRETREATMENT AS AN AIR POLLUTION CONTROL TECHNIQUE

FINAL REPORT

by

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Contract No. 68-03-3149
Task No. 12-5

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U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

274

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/2-86/028	**2.**	**3. RECIPIENT'S ACCESSION NO.** PB86 1720957AS
4. TITLE AND SUBTITLE Preliminary Assessment of Hazardous Waste Pretreatment as an Air Pollution Control Technique		**5. REPORT DATE** March 1986
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) J. J. Spivey, C. C. Allen, D. A. Green, R. L. Stallings and J. P. Wood		**8. PERFORMING ORGANIZATION REPORT NO.** 472U-2500-15
9. PERFORMING ORGANIZATION NAME AND ADDRESS Research Triangle Institute P.O. Box 12194 Research Triangle Park, NC 27709		**10. PROGRAM ELEMENT NO.**
		11. CONTRACT/GRANT NO. 68-03-3149, Task 12-5
12. SPONSORING AGENCY NAME AND ADDRESS Hazardous Waste Engineering Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268		**13. TYPE OF REPORT AND PERIOD COVERED** July 25, 1983 - July 31, 1984
		14. SPONSORING AGENCY CODE EPA/600/12
15. SUPPLEMENTARY NOTES		

16. ABSTRACT

This report evaluates twelve commercially available treatment techniques for their use in removing volatile constituents from hazardous and potentially hazardous waste streams. A case study of the cost of waste treatment is also provided for each technique. The results show that air stripping or evaporation coupled with carbon adsorption of the off gases; steam stripping; and batch distillation are the most widely applicable pretreatment techniques. The cost-effectiveness of pretreatment varies widely with waste stream characteristics and type of pretreatment, with typical values being between $55 and $1,800 per megagram of volatile removed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	**19. SECURITY CLASS (This Report)** UNCLASSIFIED	**21. NO. OF PAGES** 275
	20. SECURITY CLASS (This page) UNCLASSIFIED	**22. PRICE**

NOTICE

The information in this document has been funded wholly or in part by the United State Environmental Protection Agency under Contract No. 68-03-3149 to Research Triangle Institute. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document.

FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs, and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

The subject of this report is the pretreatment of hazardous waste streams which contain volatile constituents for the purpose of removing these volatile constituents prior to further treatment, storage, and disposal at a hazardous waste management facility. The results and conclusions of this report can be used to determine the technical and economic feasibility of pretreatment of various hazardous waste streams to remove volatile compounds. Those who would find this report of use include treatment, storage, and disposal facility (TSDF) owners/operators, hazardous waste regulatory personnel, and engineers concerned with emissions from TSDFs and engineering unit operations to reduce these emissions. For further information, contact the Alternative Technologies Division, Hazardous Waste Engineering Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

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ABSTRACT

There are many hazardous or potentially hazardous waste streams that contain volatile compounds that can be emitted to the atmosphere during waste storage, treatment, and disposal. One way to minimize or eliminate these emissions is to pretreat wastes to remove these compounds.

This report evaluates twelve commercially available treatment techniques for their use in removing volatile constituents from hazardous and potentially hazardous waste streams. A case study of the cost of waste treatment is also provided for each technique. The results show that air stripping or evaporation coupled with carbon absorption of the of the offgases; steam stripping; and batch distillation are the most widely applicable pretreatment techniques. The cost-effectiveness of pretreatment varies widely with waste stream characteristics and type of pretreatment, with typical values being between $55 and $1,800 per megagram of volatile removed.

This report was submitted in partial fulfillment of EPA Contract 68-03-3149, Task 12-5 by Research Triangle Institute under the sponsorship of the U.S. Enviromental Protection Agency. This report covers a period from August 1983 to July 1984, and work was completed as of October 1984.

CONTENTS

Section Page

Foreword . . . iii
Abstract . . . iv
Figures . . . viii
Tables . . . x

1 Introduction . . . 1
1.1 Purpose . . . 1
1.2 Indication of Problem . . . 2
1.3 Approach . . . 4
1.4 Study Limitation . . . 7

2 Conclusions . . . 9
2.1 Waste Stream Data Bases . . . 9
2.2 Emissions Modeling . . . 10
2.3 Cost of Pretreatment . . . 10

3 Review of Classification Schemes and Hazardous Waste Data Bases . . . 15
3.1 Introduction . . . 17
3.2 Discussion of Available Data Bases . . . 24
3.2.1 Office of Solid Waste, TSDF National Survey . . . 24
3.2.2 Waste Environmental Treatment (WET) Model Hazardous Waste Data Base . . . 25
3.2.3 Assessment of Air Emissions from Hazardous Waste TSDFs . . . 28
3.2.4 Survey of Potential Hazardous Waste Streams . . . 29
3.3 Summary . . . 29

4 Treatment, Storage, and Disposal Facility (TSDF) Characterization . . . 31
4.1 The Domestic TSDF Population . . . 31
4.2 Treatment, Storage, and Disposal Practices . . . 35

5 Pretreatment Techniques . . . 38
5.1 Steam Stripping . . . 46
5.1.1 Introduction . . . 46
5.1.2 State of the Art . . . 47
5.1.3 Example Case . . . 51
5.1.4 Advantages and Disadvantages . . . 52
5.1.5 Recommendations for Further Study . . . 52
5.2 Chemical Oxidation . . . 53
5.2.1 Introduction . . . 53
5.2.2 State of the Art . . . 53
5.2.3 Example Case . . . 59
5.2.4 Advantages and Disadvantages . . . 61
5.2.5 Recommendations for Further Study . . . 66

CONTENTS (continued)

Page

5.3 Adsorption 66
    5.3.1 Introduction 66
    5.3.2 Liquid Phase Carbon Adsorption. 67
    5.3.3 Resin Adsorption. 96
    5.3.4 Air Stripping/Adsorption. 109
    5.3.5 Evaporation/Adsorption. 115
5.4 Biological Treatment 120
    5.4.1 Introduction 120
    5.4.2 State of the Art 124
    5.4.3 Example Case 126
    5.4.4 Advantages and Disadvantages 130
    5.4.5 Recommendations for Further Study 131
5.5 Ozonation/Radiolysis 132
    5.5.1 Introduction 132
    5.5.2 State of the Art 137
    5.5.3 Example Case 145
    5.5.4 Advantages and Disadvantages 145
    5.5.5 Recommendations for Further Study 149
5.6 Distillation 149
    5.6.1 Introduction 149
    5.6.2 State of the Art 150
    5.6.3 Example Case 160
    5.6.4 Advantages and Disadvantages 162
    5.6.5 Recommendations for Further Study 163
5.7 Wet Oxidation 164
    5.7.1 Introduction 164
    5.7.2 State of the Art 165
    5.7.3 Example Case 171
    5.7.4 Advantages and Disadvantages 174
    5.7.5 Recommendations for Further Study 174
5.8 Solvent Extraction 174
    5.8.1 Introduction 174
    5.8.2 State of the Art 175
    5.8.3 Example Case 180
    5.8.4 Advantages and Disadvantages 181
    5.8.5 Recommendations for Further Study 181
5.9 Physical Separation 181
    5.9.1 Introduction 181
    5.9.2 State of the Art 182
    5.9.3 Example Case 190
    5.9.4 Advantages and Disadvantages 192
    5.9.5 Recommendations for Further Study 195

6 Pretreatment-Waste Stream Applicability 196

7 References 203

CONTENTS (continued)

Section Page

Appendix A Process Economics 209

Appendix B Atmospheric Emission from Cooling Towers 225

Appendix C 1983 WET Model Waste Data Base 246

FIGURES

Number Page

4-1 Regional disbribution of treatment, storage, disposal facilities in 1981 32

4-2 Number of commercial versus other TDF facilities 33

4-3 Number of facilities with treatment, storage, and/or disposal in 1981 34

4-4 Quantities of hazardous waste disposal in 1981 37

5-1 Process flow sheet and mass balance for steam stripping pretreatment of WET stream 02.01.04 48

5-2 Treatment of paint stripping effluent with hydrogen peroxide 55

5-3 Process flow sheet for ozone pretreatment of WET stream 01.02.04 61

5-4 Process flow sheet for chlorine pretreatment of WET stream 01.02.02 64

5-5 Steps in carbon adsorption 73

5-6 Carbon adsorber configurations 75

5-7 Process flow sheet for carbon adsorption pretreatment to remove volatile constituents from hazardous waste . . . 92

5-8 Process flow sheet for resin adsorption pretreatment to remove volatile constituents from hazardous waste . . . 103

5-9 Process flow sheet for air stripping/carbon adsorption pretreatment to remove volatile constituents from hazardous waste 112

5-10 Process flow sheet for evaporation/carbon adsorption pretreatment to remove volatile constituents from hazardous waste 118

5-11 General process diagram for anaerobic biological treatment 123

FIGURES (continued)

Number Page

5-12 Process flow sheet for anaerobic biological treatment of WET stream 02.02.12 128

5-13 Process flow sheet for five ozonation/radiolysis processes 139

5-14 Process flow sheet for ozonation pretreatment of quench blowdown from ethylene production by cracking of heavy liquids 146

5-15 Process flow sheet for continuous fractional distillation column 151

5-16 Process flow sheet for simple batch distillation scheme . 153

5-17 Process flow sheet for batch distillation with rectification 155

5-18 Process flow sheet for example case of distillation pretreatment 161

5-19 Basic process flow sheet for wet oxidation 168

5-20 Wet air oxidation plant for Hoerner, Waldorf, Ontonagon, Michigan 169

5-21 Process flow sheet for wet oxidation pretreatment of WET stream 02.02.21 172

5-22 Process flow sheet for treatment WET stream 02.01.03 by solvent extraction with di-isopropyl ether (DIPE) . . 176

5-23 Process flow sheet for sedimentation 185

5-24 Process flow sheet for dissolved air flotation 186

5-25 Process flow sheet for sand filtration 187

5-26 Process flow sheet for vacuum filtration 187

5-27 Process flow sheet for centrifugation 188

5-28 Process flow sheet for a hydrocyclone 188

5-29 Process flow sheet for pretreatment by centrifugation of WET stream 05.01.03 (sludge from tin plating) 193

TABLES

Number Page

2-1 Appropriate Pretreatment Process by Waste Type 11

2-2 Hazardous Waste Pretreatment: Estimate of Process Economics for Selected Candidate Pretreatment Techniques 12

3-1 Some Hazardous Waste Classification Schemes Developed Primarily for Regulatory Purposes 17

3-2 Waste Classification by Listing of Waste Type 19

3-3 Example of UCD Waste Categories 20

3-4 Example of a Numerical Ranking Scheme for Hazardous Waste Classification 22

3-5 Waste Streams Listing from the WET Model Hazardous Waste Data Base 26

4-1 Number of Facilities Using Selected Treatment, Storage and Disposal Processes 36

5-1 Technologies Evaluated as Potential Pretreatment Options 39

5-2 Performance Data for Steam Stripping of Kraft Mill Condensates 50

5-3 Applications of Chemical Oxidation 60

5-4 Mass Balance for Ozone Treatment of Stream 01.02.04 . . 63

5-5 Mass Balance for Alkaline Chlorination of Stream 01.02.02 65

5-6 Characterization of Carbon Contracting Methods for Hazardous Waste Treatment 76

5-7 Summary of Industrial Sources Using Granular Activated Carbon Systems 84

5-8 Full-Scale Activated Carbon Systems Treating Organic Chemical Wastes 85

5-9 Industrial Wastewater Treatment Granular Activated Carbon Installations 87

TABLES (continued)

Number		Page
5-10	Composition of WET Stream 02.02.14	91
5-11	Capital and Operating Costs for Carbon Adsorption Pretreatment with Thermal Reactivation of the Carbon for WET Model Stream 02.02.14	95
5-12	Capital and Operating Costs for Resin Adsorption Pretreatment with Solvent and Waste Recovery for WET Model Stream 02.02.16	106
5-13	Capital and Operating Costs for Air Stripping/ Adsorption Treatment System for Waste Stream 02.02.20 .	114
5-14	Capital and Operating Costs for Evaporation/GAC Adsorption Treatment of Waste Stream 03.04.14	121
5-15	Existing Anaerobic Treatment Sites	127
5-16	Treatment of Wet Stream 02.02.12 Heavy Ends from Ethylene Oxide Production from Ethylene	129
5-17	BaP Decomposition by Gamma Radiation	135
5-18	Effect of Oxygen on the Ultraviolet-Induced Decomposition of BaP in Solution	135
5-19	Waste Stream Requirements for Ozonation/Radiolysis . . .	141
5-20	Materials Suitable for Low Energy (UV) Photolysis . . .	143
5-21	Operating Costs (1980$) and Energy Requirements for Ozone Generation	147
5-22	Ozonation/Radiation	148
5-23	Partial Listing of Independent Precessors and Waste Treatment Distillers	157
5-24	Waste Forms That Can Be Distilled	158
5-25	Waste Types That Can Be Distilled	159
5-26	Recent Research on the Application of Wet Oxidation to Aqueous Waste Streams	166
5-27	Mass Balance for Wet Oxidation Treatment of Amiben® Wastewater	170

TABLES (continued)

Number Page

5-28 Mass Balance for Wet Oxidation of WET Stream 02.02.21 . 173

5-29 Applications Using Physical Separation Equipmemt 191

5-30 Mass Balance for Treatment of WET Stream 05.01.03 by Centriguation 194

6-1 Waste Stream-Pretreatment Applicability 195

SECTION 1

INTRODUCTION

Research Triangle Institute (RTI) has undertaken a preliminary assessment for the Hazardous Waste Engineering Research Laboratory of the U.S. Environmental Protection Agency of the technical and economic feasibility of treatment techniques to remove volatile compounds from hazardous waste streams. This study is prompted by increasing concern over air emissions from treatment, storage and disposal facilities (TSDFs) which manage hazardous wastes. Operations at TSDFs that emit volatile compounds include such processes as aerated impoundments, surface impoundments, land treatment facilities, landfills, storage tanks, drum handling operations and general process operations. Treating wastes to remove volatiles before the wastes enter these processes (i.e., waste "pretreatment") is one option for reducing volatile emissions from these processes.

1.1 PURPOSE

The purpose of this study is to conduct a preliminary assessment of the technical and economic feasibility of various pretreatment techniques for the removal of volatile constituents from hazardous waste streams. As a preliminary assessment, the study is not expected to be an end in itself. It was intended to develop a methodology for evaluating alternative pretreatment techniques and to make an initial identification of those techniques that are applicable to a wide variety of waste stream types, are cost-effective, and are commercially available. Because this is a preliminary assessment, the conclusions drawn are general, and application to specific cases should be done with care, particularly given the complexity of hazardous waste and its treatment.

1.2 INDICATION OF PROBLEM

This study is the result of increasing concern over the potential adverse health and environmental consequences associated with emissions of volatile substances. Such emissions from TSDFs are of particular interest. According to preliminary unpublished results from an EPA national survey of TSDFs (US EPA 1983a) conducted in 1981, there are about 4,820 TSDFs in this country managing a total of about 151 billion liters, or approximately 100 million Mg, of hazardous waste annually. While no comprehensive estimate of the total volatile emissions from all domestic TSDFs has been reported, at least one estimate has been made. Preliminary estimates by Breton et al. (1983) were made for nationwide emissions of 54 selected volatile compounds regulated under the Resource Conservation and Recovery Act (RCRA). They have also estimated total emissions of all volatile organic compounds (VOCs). Their estimate does not include facilities that have not yet filed for Part A permits or sites regulated under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). Total nationwide emissions of the 54 RCRA regulated chemicals from TSDFs were estimated at 1.6 million Mg per year. Total nationwide VOC emissions from TSDFs were estimated to be between 1.6 and 5.4 million Mg per year, while total VOC emissions from all sources was estimated at about 22.3 million Mg per year. Consequently, emissions from TSDFs may represent as much as 19.5 percent of total nationwide VOC emissions. These results, although preliminary and based on limited data, indicate that emissions of volatile compounds from TSDF may be significant.

There are a number of sources within TSDFs from which volatile emissions can be emitted. These sources include the following:

- Aerated impoundments--mechanically agitated liquids in direct contact with the atmosphere
- Surface impoundments--quiescent liquids or sludges in direct contact with the atmosphere
- Landfills--liquids, solids, or sludges usually covered with thin soil layers
- Land treatment--liquids or dilute sludges applied mixed with surface soil

- Cooling towers--liquids in direct contact with the atmosphere while flowing within a conventional cooling operation
- Storage tanks--open or covered tanks containing (usually) liquids
- Drum handling--physical handling operations during which drums may be opened or leaking drums moved
- General process operations--materials transfer in open containers, or any other operation during which the waste is exposed directly to the atmosphere.

With the exception of the cooling towers, potential emissions from these sources have been described elsewhere (Breton et al. 1983). A discussion of cooling tower emissions is provided in Appendix B. Emissions from these processes can vary considerably and are dependent upon a number of factors such as residence time of the waste, area of waste exposed to the atmosphere, and process temperature. Characterizing TSDF emissions sources and predicting the rate at which they may release volatile compounds is further complicated by the wide variety of waste streams which many of them handle.

There are a number of ways of controlling emissions from these sources. The ways can be grouped into four categories: pretreatment, in situ control, process design or operation changes, and post-treatment (Ehrenfeld 1984). Pretreatment, the subject of the present report, involves treating the waste at its point of generatin or as it enters a TSDF in order to remove the volatile constituents of the waste so that they will not be released by some other process at the TSDF. For example, air stripping could be used to remove a slightly soluble volatile from an aqueous stream, and the off gases could then be incinerated. In situ controls act directly upon a waste stream when it is in a TSDF process to reduce the potential for volatiles physically leaving the waste. An example of an in situ control would be the use of an immiscible liquid on the surface of a surface impoundment to impede the mass transfer of volatiles from the waste in the impoundment to the atmosphere. Process design changes may involve changes in process construction, such as using deeper impoundments with smaller surface areas to decrease the waste-to-atmosphere interface. Or, a change in the operation of a land treatment site to using subsurface injection instead of surface spreading could be made to reduce emissions. Post treatment control involves the capture and subsequent disposal (or reuse) of emissions from a TSDF process. For example, a surface impoundment could be covered with an inflatable dome and the volatile gases vented through a column of activated charcoal.

When considering the appropriate emissions control to be used on a process at a given TSDF, the cost-effectiveness of the options available for the process at that site must be considered, along with the possibility that a technique like pretreatment may reduce emissions from several processes at the site. Because of the numerous processes and controls that must be considered, a comparison between the cost-effectiveness of pretreatment and controls falling in the three other categories was not undertaken in the present study. Such a comparison is being made by others using the pretreatment cost estimates developed here (Ehrenfeld 1984).

1.3 APPROACH

RTI examined potential chemical engineering techniques for pretreating hazardous wastes and selected 12 broad techniques as being the most applicable. These are

- Steam stripping
- Chemical oxidation
- Carbon adsorption
- Resin adsorption
- Air stripping/adsorption
- Evaporation/adsorption
- Biological treatment
- Ozonation/radiolysis
- Distillation
- Wet oxidation
- Solvent extraction
- Physical separation

Other potential techniques were not considered appropriate for pretreatment with the specific intention of removing volatiles. Also excluded were technques that are used primarily for ultimate destrucion, such as incineration and pyrolysis.

To evaluate pretreatment technology for removing volatile constituents, reasonably detailed data on stream composition and physical properties are required. Thus, one major task of this study is an in-depth evaluation of hazardous waste classification schemes and existing hazardous waste data bases. It was necessary to determine if any existing data base contained sufficient information to permit a valid assessment concerning the compatibility of waste streams with specific pretreatment technologies. A comprehensive data base containing waste stream composition and generation rate data was needed for this study. An exhaustive and complete data base of this sort is not currently available. RTI's review of existing hazardous waste stream data bases indicated that the Waste Environmental Treatment (WET) Model data base (U.E. EPA 1983b) was best suited for use in assessing the compatibility of pretreatment techniques with specific waste streams. Thus, conclusions based on the methodology of this report are limited by the data base chosen. The identification and evaluation of alternative waste characterization data bases is reported in Section 3, including discussions concerning the limitations of the WET Model data base. It was also noted that the WET Model data base includes listed and unlisted waste streams.

The definition of "volatile constituent" used in the report is broader than those found in other contexts of environmental science. This was done because when the study was initiated it was not known what compounds were of greatest concern when emitted from TSDF's. In particular, one probably cannot just take the physical property of volatility into account to identify emitted compounds of significant concern, but also must factor in the potential health effects. With this in mind, it was decided that when evaluating waste streams in the WET Model data base, all those compounds listed as a Constituent of Concern in a given waste stream and known to have a significant vapor pressure should be analyzed. Generally this vapor pressure was over 0.1 mm Hg at 25° C, but in some cases compounds of lower vapor pressure were included because they might have significant health impacts. This approach to scoping the problem leads to an analysis of compounds with a very wide range of physical characteristics that reflect volatility (e.g., vapor pressure of the pure compound, or Henry's law constant). For example, one result of this definition is that mercury is analyzed. More importantly, organic compounds such as phenol, which are considered to be semivolatiles in the field of water quality, are included under the broad term of volatile constituent in this report. It was felt that because the problem of TSDF volatile emissions was just beginning to be scoped, it was better to be overly inclusive in the analysis than to exclude compounds that ultimately might prove to be significant even though they had low vapor pressures.

The impact of adopting waste stream pretreatment for volatile constituent recovery cannot be estimated without some knowledge of emissions that currently occur at existing TSDFs. Thus, another important task was to characterize existing TSDFs; this included investigating prevalent methods of treatment and disposal and their associated emissions, as well as gathering descriptive statistics concerning TSDFs. Section 4 is a discussion of the available information on TSDF characteristics. Data from the WET Model were used in conjunction with published data and engineering judgement to match waste streams from the WET Model with candidate pretreatment technologies (see Sections 5 and 6). In addition, WET Model data on waste generation rates were used to estimate the appropriate equipment scale (Section 5). Material balances, energy balances, and equipment cost estimates based on this scale could then be used to estimate economic parameters such as the cost effectiveness associatd with each technology. When possible, data from the other sources (as mentioned above) were used to supplement data from the WET Model.

Section 5 of the report is divided into discussions of each of the techniques that were chosen for assessment. There is a description of how each technique operates, as well as its current state of development and its use in industry and in waste disposal. Expected efficiencies for removing volatiles from waste streams are estimated.

For each pretreatment technique, there is a set of hazardous waste stream characteristics (or criteria) that determine whether the technique is applicable for that stream. Using these criteria, an appropriate WET Model stream has been selected, and a detailed example has been prepared to show how the given pretreatment technique might be used for this specific WET stream. The capital and operation and maintenance costs for treating the example stream are determined, along with the costs of controlling treatment residuals and the credits from any residuals that can be recycled. (Detailed cost tables for each example are provided in Appendix A of the report). From this data, the unit cost ($/kg stream treated) and the cost-effectiveness

($/kg of volatile removed) are calculated.

In Section 6 of the report, the compatibility of 72 of the WET Model wsate streams with each of the pretreatment techniques is graded on a scale ranging from those combinations of streams and techniques which have been "demonstrated" on a commercial scale to those which are "inapplicable" because there is no conceptually valid basis for expecting that volatile removal from a particular stream can be accomplished using a particular pretreatment technique.

1.4 STUDY LIMITATIONS

This report documents a preliminary assessment of a very complex topic, and, consequently, the detailed parts of the analysis must be used with caution. There are a number of limitations and weaknesses in the analysis resulting from limited available information and study resources which may effect the results. The limitations, however, should primarily affect the details of applying pretreatment to specific TSDFs and of determining pretreatment emissions reductions that can be achieved, and should not significantly affect the conclusions about the general applicability of specific pretreatment techniques to various categories of waste streams.

The hazardous waste streams considered here are limited in number. The 1983 version of the WET Model data base that was used represents less than half the streams that are listed in a recently updated version of that data base. On the other hand, the WET Model data base includes potentially hazardous as well as listed waste streams. Therefore, some non-listed waste streams are considered in this report. In addition, there have been since some modifications to the quantities (and, in some cases, the species) that were listed for individual waste streams. Therefore, the quantitative waste stream data presented here should be used with caution.

Finally, it should be noted that each of the cost-effectiveness calculations performed in Section 5 and Appendix A were done for a single waste stream of a single size. A different stream was chosen to develop costs for each treatment technique. Cost-effectiveness will vary with the size of the pretreatment process because of economics of scale and may change with waste stream characteristics. Therefore, one must be careful when making direct comparisons between the cost-effectiveness of the various pretreatment techniques presented there to account for these differences.

SECTION 2

CONCLUSIONS

The following conclusions have been drawn from this preliminary assessment of techniques that can be used for removing volatiles from hazardous waste streams. Because waste stream charaterization and treatment cost were integral parts of this assessment, conclusions about these topics are also included.

2.1 WASTE STREAM DATA BASES

Existing waste stream classification schemes that use a single methodology (e.g., listing of waste properties) do not contain the data required to perform thorough technical and economic assessments of candidate pretreatment technologies. A review of available literature and data bases suggests that a classification scheme that combines waste property and waste type listings is best suited for this and subsequent studies of a similar nature. An ideal scheme for this study would contain the following types of data:

- Waste properties, including reasonably detailed data on the stream composition, to facilitate an assessment of (1) the volatile nature of the stream, and (2) waste stream/pretreatment technology compatibility.
- A listing of wastes streams by source to facilitate waste-specific identification.
- Production-related data to allow a preliminary estimate of the appropriate pretreatment system design scale amd potential magnitude of volatile emissions.

RTI evaluated the available compilations of hazardous waste stream composition and generation rate information to find the one most suitable for this study. The Waste Environmental Treatment (WET) Model (U.S. EPA 1983b) was judged to have the most pertinent information for an engineering assessment of this type; it is also the most comprehensive, in spite of its limitations.

2.2 PRETREATMENT TECHNIQUES

There are a number of alternative processes available for treatment of most hazardous waste streams. This fact is demonstrated in Table 6-1 of this report, in which a matrix matches the 12 pretreatment techniques with the 72 waste streams considered here. Based on this matrix, the following pretreatment techniques are considered most applicable for removing volatile constituents from the WET Model waste streams, considering cost, range of waste streams which could be pretreated, and the extent to which the technology has been demonstrated:

- Carbon adsorption (liquid and gas phase)
- Steam stripping
- Batch distillation

A distinction can be made between pretreatment processes which are applicable at the site of generation and processes which could be used at a TSDF that accepts waste materials from a variety of sources. Techniques which are best suited to steady stream composition and flow include continuous distillation, solvent extraction, and, to some extent, biological treatment. At a typical commercial TSDF, the waste streams are generally not segregated by source. Thus, pretreatment using the three above-mentioned techniques, which possess the capability of handling a variety of waste types as opposed to other techniques discussed in Section 5, is likely to be most applicable at TSDFs.

For any given waste stream category (e.g., aqueous wastes), there are pretreatment techniques which are most appropriate. These are summarized in Table 2-1.

2.3 COST OF PRETREATMENT

The cost-effectiveness of pretreatment varies greatly in the example cases considered here. Cost scenarios and estimated cost-effectiveness are presented in Table 2-2. The assumptions associated with these cost estimates are discussed in Appendix A. For these cases, the costs range from approximately $55/Mg of volatile removed (for a large, relatively concentrated stream) to approximately $1,800/Mg (for a relatively small, dilute stream).

TABLE 2-1. APPROPRIATE PRETREATMENT PROCESS BY WASTE TYPE

Waste type	Applicable pretreatment process
Organic liquids	Distillation
Aqueous, up to 20% organic	Steam stripping Solvent extraction
Aqueous, less than 2% organic	Steam stripping Carbon adsorption Resin adsorption Air stripping with carbon adsorption Ozonation/radiolysis Wet oxidation Biological treatment
Sludge with organics	Air stripping with carbon adsorption Ozonation/radiolysis Wet oxidation Chemical oxidation Evaporation with carbon adsorption
Some sludge in organic or aqueous stream	Physical separation

TABLE 2-2: HAZARDOUS WASTE PRETREATMENT: ESTIMATE OF PROCESS ECONOMICS FOR SELECTED CANDIDATE PRETREATMENT TECHNIQUES[a]

Technology	Basis of estimate	Estimated unit cost, January 1983 dollars	Estimated cost effectiveness, January 1983 dollars
Adsorption, carbon	WET model stream 02.02.14 (quench blowdown from ethylene production). 17,751 kg/hr @ 0.4 wt. % toluene, 0.3 wt. % phenol, 0.5 wt. % benzene. 330 day/yr operation @ 24 hr/day. 100% removal of toluene, phenol, and benzene.	$0.0192/kg treated	$1.60/kg organic removed
Adsorption, resin	WET model stream 02.02.16 (Decanter wastes from phenol production). 14,583 kg/hr @ 2 wt. % phenol, 90 wt. % water. 330 day/yr operation @ 24 hr/day. 100% removal of phenol.	$0.0061/kg treated	$0.31/kg phenol removed
Biological treatment	WET model stream 02.02.12 (Heavy ends from ethylene oxide production) 15.8 percent acetaldehyde produced at 2,800 kg/day.	$0.0080/kg treated	$0.068/kg organic removed
Distillation	WET model stream 03.01.90 (spent solvents). 454 kg/hr @ 80 wt. % toluene, 20 wt. % hexane. 2,800 hr/yr operation. Overhead product @ 95 mol % hexane, bottoms product @ 95 mol % toluene.	$0.05/kg treated	$0.251/kg organic removed
Evaporation (with carbon adsorption)	WET model stream 03.04.14 (distillation cut from acetaldehyde production by ethylene oxidation). 24,000 kg/day. 16.2 wt. % acetaldehyde, 11.7 wt. % chloroacetaldehyde, 2 wt. % chloroform, and 2 wt. % formaldehyde. 330 day/yr operation @ 24 hr/day. 100% removal of all species.	$0.069/kg treated	$0.14/kg organic removed
Oxidation, chemical	10^6 gal/day of coke plant wastewater containing phenol and ammonia. 350 day/yr operation @ 24 hr/day.	$0.0069/kg treated	$91/kg cyanide removed
Oxidation, wet	WET stream 02.02.21 (acetophenone column separator from phenol production by cumene hydroperoxide). 12,500 kg/hr contain 1 wt. % phenol in aqueous soln. 350 day/yr operation @ 24 hr/day.	$0.0125/kg treated	$1.39/kg phenol removed

Footnotes at end of table.

(continued)

TABLE 2-2 (continued)

Technology	Basis of estimate	Estimated unit cost, January 1983 dollars	Estimated cost effectiveness, January 1983 dollars
Ozonation	WET model stream 02.02.14 (quench blowdown from ethylene production). 17,751 kg/hr @ 0.4 wt. % toluene, 0.3 wt. % phenol, and 0.5 wt. % benzene. 350 day/yr operation @ 24 hr/day. 95% removal of toluene, phenol, and benzene.	$0.02/kg treated	$1.81/kg organic removed
Physical separation via bowl centrifuge	WET model stream 05.01.03 (sludge from tin plating mill operations). 8,200 kg/day @ 10 wt. % solids. 350 day/yr operation @ 24 hr/day. ~99% solids removal.	$0.008/kg treated	b
Solvent extraction	WET model stream 02.01.03 (phenol-formaldehyde solution from plastics production) 1,600 kg/hr @ 5 wt. % phenol, 2 wt. % formaldehyde, 90 wt. % water. 350 day/yr operation @ 24 hr/day.	$0.0024/kg treated	$0.055/kg phenol removed
Stripping, air (with carbon adsorption)	WET model stream 02.02.20 (caustic scrubber effluent from perchloroethylene and carbon tetrachloride production). 500 kg/hr @ 1.3 wt. % CCl_4 and 88.8 wt. % water. 330 day/yr operation @ 24 hr/day. 100% removal of CCl_4.	$0.018/kg treated	$1.40/kg CCl_4 removed
Stripping, steam	WET model stream 02.02.14 (quench blowdown from ethylene production). 17,750 kg/hr @ .4 wt. % toluene, .3 wt. % phenol, .5 wt. % benzene. 350 day/yr operation @ 24 hr/day.	$0.026/kg treated	$2.62/kg organic removed

[a] Capital costs are annualized at 10% over 10 years.

[b] This process is used in combination with other pretreatment processes.

The cost-effectiveness for removal of volatiles from the waste stream will not necessarily represent the cost-effectiveness of reducing the mass of emissions released from a given source. There will be some sources for which the emissions rates are sufficiently high and the waste residence time sufficiently long that all volatiles will be emitted (unless there is some competing mechanism for destroying, e.g., through biological degradation). In such cases, the cost-effectiveness of volatile removal is approximately equal to the cost-effectiveness of pretreatment as an emissions control. For sources such as storage tanks which have low emissions rates the use of pretreatment for emissions control will be less cost effective.

SECTION 3

REVIEW OF CLASSIFICATION SCHEMES AND HAZARDOUS WASTE DATA BASES

3.1 INTRODUCTION

A procedure to classify hazardous wastes is both necessary and desirable when assessing issues related to hazardous waste treatment, storage, and disposal. The use of a classifiation scheme provides a common basis for comparing various treatment, storage, and disposal technologies, and ensures that such comparisons are meaningful. One task of this study was to assess available waste categorization schemes to determine which, if any, was best suited for evaluating the applicability of pretreatment technologies to various waste streams.

Unfortunately, hazardous wastes defy easy classification into discrete "types." This is due primarily to the large variability (in terms of physical properties and composition) displayed by hazardous waste streams. The universe of hazardous waste streams is best described as a continuum that is not easily subdivided. For this reason, past efforts to develop waste classification schemes have varied in scope and content depending upon the needs of the user or developer.

For an effective assessment of the technical and economic applicability of pretreatment technologies for removing volatile constituents from various waste streams, a classification scheme that provides two types of information is desirable:

1. Data that will allow a complete assessment of the physical and chemical nature of the waste stream, especially:

    - to potential volatility of the stream, and

    - the compatibility of the waste stream with proposed pretreatment techniques.

2. Hazardous waste stream volumetric production rates (e.g., kg/day) that can be used to make preliminary estimates of equipment scale.

While numerous waste classification schemes have been developed and implemented, none provides the detailed chemical and physical information necessary for a study of this type.

Established waste classification schemes have used one or a combination of several available techniques. As suggested earlier, the technique(s) employed have depended to a large extent on the needs and interests of the developer. The three approaches most commonly employed are the following (Metry 1978):

- Categorization by waste properties, e.g. toxicity, flamability, etc.
- Categorization by waste types, e.g., polychlorinated aromatics
- Numerical ranking of wastes based upon a mathematical ranking system (a quantitative approach based on the first approach above).

Table 3-1 lists 20 hazardous substance classification schemes that were developed primarily for regulatory purposes. All of these schemes utilize a listing of waste properties. In fact, each of these schemes uses toxicological criteria to determine whether or not a substance should be clasified as hazardous (Kohan 1975). Such classification schemes may be of some use at the present study, in that an estimate of waste stream volatility might be made from other waste stream characteristics, e.g., flammability. However, what quantitative waste stream data is provided in these data bases usually cannot be directly related to the physical and chemical parameters required for a complete assessment of waste stream treatment. In addition, such schemes generally do not contain the information required to establish an appropriate equipment scale (capacity) for pretreatment technologies.

Classifications according to waste type have the inherent advantage of allowing easy waste-specific identification (Kohan 1975). Such schemes typically take two forms, namely:

TABLE 3-1. SOME HAZARDOUS WASTE CLASSIFICATION SCHEMES DEVELOPED PRIMARILY FOR REGULATORY PURPOSES[a]

System	Classification criteria[b]											
	1	2	3	4	5	6	7	8	9	10	11	12
Title 15, U.S. Code, Sec. 1261	X	X		X			X	X	X			X
CPSC-Title 16, CFR, Part 1500	X	X		X			X	X	X			X
Food, Drug, and Cosmetic Act	X									X	X	X
DOT-Title 49, CFR, Parts 100-199	X	X	X	X		X	X	X				X
Pesticides-Title 40, CFR, Part 162	X	X								X	X	
Ocean Dumping-Title 40, CFR, Part 227	X									X	X	X
NIOSH-Toxic Substances List	X										X	
Drinking Water Standards	X									X	X	
FWPCA Sec. 304 (a)(1)	X									X	X	
Sec. 307 (a)	X									X	X	X
Sec. 311 (b)(2)(A)	X											X
Clean Air Act-Sec. 112	X							X			X	
California State List	X	X	X	X				X	X			
National Academy of Sciences	X	X			X							
TRW Systems Group	X	X	X	X			X			X		X
Batelle Memorial Institute	X	X	X		X	X	X	X		X	X	
Booz-Allen Applied Research, Inc.	X	X	X		X							X
Dept. of the Army	X											
Dept. of the Navy	X	X	X	X	X	X	X					
National Cancer Institute	X									X	X	X

[a] Source: Kohan (1975).

[b] Classification criteria key:

1. Toxicological	7. Radioactive
2. Flammability	8. Irritant
3. Explosive	9. Strong sanitizer
4. Corrosive	10. Bioconcentration
5. Reactivity	11. Carcinogenic, mutagenic, teratogenic
6. Oxidizing material	12. Sufficient quantity

- Classification based upon the generic chemical nature of the waste, e.g., aqueous organics,
- Classification based upon the source of the waste stream, e.g., phenolic sludge from the production of plastics.

The classification scheme presented in Table 3-2 is a good example of the first case above. The chemical and physical nature of the waste are considered in formulating the various waste groups. This particular classification scheme was developed by a commercial TSDF to describe the type and nature of the wastes handled (Exner 1978).

The University of California-Davis (UCD) waste categorization utilizes both of the classification schemes mentioned above. In the UCD scheme, waste categories are based on the chemical/physical nature of the waste in conjunction with the waste source (Toxic Waste Assessment Group 1981). Table 3-3 presents a listing of several UCD waste categories under the overall heading of inorganics.

The obvious drawback (for this study) of classification schemes that rely solely on waste properties is the probable lack of data that would allow one to establish an appropriate equipment scale and associated process design for candidate pretreatment technologies. However, such schemes could be used to identify waste streams that could be pretreated. In addition, schemes such as that presented in Table 3-2 generally do not provide data necessary to estimate the volatile content of the waste with any reasonable degree of certainty.

Numerical ranking of wastes for the purpose of waste classification incorporates the use of weighing factors that are applied to waste criteria such as toxicity, flammability, etc. (Metry 1978). Typically, a single numerical rating is obtained by using a mathematical combination of weighted criteria. One such system, developed by Booz-Allen Applied Research, is illustrated in Table 3-4. In this system, the potential effects of human toxicity, flammability/explosion potential, and ecological impact are rated with respect to air exposure, water exposure, and land exposure. The sum of the weighted ratings is in turn rated with respect to production (quantity generated) and distribution (type of transportation and user characteristics). The weighting factors used by Booz-Allen are not always unity (although

TABLE 3-2. WASTE CLASSIFICATION BY LISTING OF WASTE TYPE[a]

Group	Classification	Example
I	Aqueous Inorganic Liquid	
	Nonmetallic salts	Na_2SO_4, $NaNO_3$
	Acid	HF, HNO_3, H_2SO_4, H_3PO_4
	Acid with heavy metals	$HNO_3 + Fe(NO_3)_2$
	Alkali	NaOH
	Alkali with heavy metals	NaOH + lead
	Cyanide	NaCN, KCN, $Cd(CN)_2$, $Zn(CN)_2$
	Reactive (bleach, sulfide)	Mercaptans, H_2S, Na_2S
	Brine	NaCl
II	Aqueous Organic Liquid	
	Biodegradable organic	Acetone, MEK, acetic acid
	General organic	Phenol
	Organic and heavy metals	
III	Organic Liquid	
	Liquid hydrocarbon	Hexane, gasoline
	Hydrocarbon with water	Jet fuel
	Chlorinated hydrocarbon	Not accepted
	Polychlorinated aromatics	Not accepted
	Other halogenated hydrocarbons	Not accepted
	Other substituted hydrocarbons	Mercaptans
	Oil (heavy hydrocarbon)	Crude oil w/light ends
	Organic w/heavy metal	Tar w/nickel catalyst
IV	Slurry/Sludge (Liquid/Solid)	
	Organic/organic	Waste oils
	Organic/heavy metals	
	Aqueous/heavy metals	Cooling tower sludge w/chromium
	Aqueous/inorganic nonmetallic	Aqueous calcium carbonate
	Aqueous/biological	Biological treatment plant sludge
	Organic/inorganic	Oil spill cleanups
	Aqueous/organic	Aqueous amines
V	Solids	
	Organic	High-molecular-weight alcohols
	Inorganic	Spent calcium chloride drying agent
	Inorganic with organic	Used insulation
	Heavy metal	Spent catalysts containing metals
	Contaminated trash	Empty chemical bags
	Organic heavy metal	

[a] Source: Exner 1978.

TABLE 3-3. EXAMPLE OF UCD WASTE CATEGORIES[a]

	Inorganics
(11)	Acidic Solutions (usually contain HCl, H_2SO_4 or HNO_3):
(111)	...with heavy metals (antimony, arsenic, barium, beryllium, boron, cadmium, chromium, copper, indium, lead, manganese, mercury, molybdenum, nickel, selenium, silver, tin, vanadium, and/or zinc)
(112)	...with other metals and non-metals (typically contain an alkali metal, e.g., Na, K)
(113)	other acidic solutions (acidic solutions not containing metals or non-metals, or acidic solutions with no component information provided)
(12)	Alkaline solutions (usually contain NaOH, KOH, or NH_4OH):
(121)	...with heavy metals (see (111) above)
(122)	...with other metals and non-metals (see (112) above)
(123)	other alkaline solutions (alkaline solutions not containing metals or non-metals, or alkaline solutions with no component information provided)
(13)	Metal-finishing solutions (from process identification on manifest, e.g., "metal plating," "pickling bath," etc.)
(131)	...acidic (per component listing)
(132)	...alkaline (per component listing)
(133)	spent pickle liquor (process identification)
(14)	Other aqueous (salt) solutions: (frequently acidic or basic solutions which are neutralized by generator, yielding a salt solution):
(141)	...with heavy metals (see (112) above)
(142)	...with other metals (see (113) above)
(143)	solution containing reactive anions (includes cyanide, sulfide, fluoride, hypochlorite, or bromate)
(144)	other aqueous solutions (aqueous solutions (14) other than (141), (142), (143), or (145))
(145)	brine (category 15, California manifest)
(15)	Inorganic solids:
(151)	inorganic solids (activated carbon, cement, etc.)
(152)	inorganic chemicals (miscellaneous salts, etc.)

(continued)

TABLE 3-3 (continued)

	Inorganics
(16)	Other inorganic wastes:
(161)	asbestos-containing wastes (per component information)
(162)	aluminum or tin wastes (per component information)
(165)	spent catalyst (usually silica-alumina or zeolite, containing trace metals and carbonaceous deposits)
(167)	unidentified inorganic wastes

[a] Source: US EPA 1982

TABLE 3-4. EXAMPLE OF A NUMERICAL RANKING SCHEME FOR HAZARDOUS WASTE CLASSIFICATION

COMPOUND: CADMIUM OXIDE

	Initial rating	Weight	Final rating
Air disposal			
Human toxic effects	3	1	3
Flame/explosion	2	1	2
Ecoeffects	2	1	2
Water disposal			
Human toxic effects	3	1	3
Flame/explosion	1	1	1
Ecoeffects	U	1	U
Soil disposal			
Human toxic effects	1	1	1
Flame/explosion	2	1	2
Ecoeffects	U	1	U
Total effects rating (sum of above)			14
Number of unknowns above			2
Maximum potential effects rating (unknowns × 3 + total effects rating)			20
Production rating			1.0
Distribution rating			0.5
Hazard extent rating (sum of production and distribution)			1.5
Hazard rating (total effects rating × hazard extent rating)			21
Maximum potential hazard rating (maximum potential effects rate and extent of hazard rating)			30

U = Unknown.

they happen to be in Table 3-4), but vary depending upon the relative significance of each criterion. Such a weighted ranking system might be of use to rank streams for investigation in the present study if waste volatility and toxicity were utilized as weighted criteria and if quantitative production data were included. Such quantitative production data would facilitate the specification of an appropriate pretreatment system scale (to be used as a basis for subsequent technical and economic analysis). No such schemes have been identified, however.

In summary, existing waste stream classification schemes that use a single methodology (e.g., listing of waste properties) do not contain the data required to perform thorough technical and economic assessments of candidate pretreatment technologies. A review of available literature and data bases suggests that a classification scheme that combines waste property and waste type listings is best suited for this and subsequent studies of a similar nature. An ideal scheme for this study would contain the following types of data:

- Waste properties including reasonably detailed data on the stream composition that will facilitate an assessment of (1) the volatile nature of the stream, and (2) waste stream-pretreatment technology compatibility.
- A listing of wastes streams by source, to facilitate waste-specific identification.
- Production-related data that will allow an estimate of the appropriate pretreatment system design scale (presumably the scale that would exist at a typical TSDF) and potential magnitude of volatile emissions.

Waste stream composition and physical properties are required to make a reasonable engineering judgment regarding the applicability of various pretreatment technologies. Economic assessments of sufficient detail can only be made after specification of the scale of the anticipated application.

3.2 DISCUSSION OF AVAILABLE DATA BASES

3.2 1 Office of Solid Waste, TSDF National Survey

There is little doubt that, following its completion and validation, the OSW-TSDF National Survey results will constitute an important source of data for studies of this type. The primary purpose of the survey is to characterize the populations of hazardous waste generators and TSDFs regulated under Subtitle C of RCRA (US EPA 1983a). A second purpose is to develop a national data base on hazardous waste management practices for use by OSW and others in the continuing development of the RCRA regulatory program. This survey is the most extensive data collection effort on hazardous waste management activities to date. The survey's sample of TSDFs is deemed sufficiently large to provide a statistically significant data base of process characteristics and waste stream management information.

Once data reduction efforts are complete, the OSW-TSDF National Survey should provide much of the background information necessary to effectively assess the quantities and disposition of various waste streams, (particularly those that have been assigned an EPA waste number), as well as potential emissions from the facilities At least two important components are missing, however: (1) even general waste characteristics are not reported (e.g., is the waste a sludge, slurry, etc.), and (2) there are no data related to waste stream volatility (e.g., vapor pressure data).

While the details of the survey are too extensive for discussion here, the following pertinent data exemplify the type of information that should be available from the survey:

- Quantity (gal/yr) of waste treated, stored, and disposed for each EPA waste number.
- Quantity (by waste number) vs. treatment, storage, or disposal technique.

Information on waste stream composition (as derived from the EPA waste number) can, in many cases, be used to assess the volatility of the waste streams. Also, since one of the primary purposes of the survey was to characterize domestic TSDFs, the survey results should be useful for determining the appropriate equipment scale for candidate pretreatment technologies.

Other data that can be used in assessing the overall effectiveness of pretreatment, e.g., data relating to emissions modeling of disposal technologies, should also be available upon completion of the project.

3.1.2 Waste Environmental Treatment (WET) Model Hazardous Waste Data Base

The 1983 version WET Model data base accounts for a total annual generation of approximately 76.8 million Mg of hazardous wastes represented by 147 waste streams (US EPA 1983b). Table 3-5 presents data for two waste streams (02.02.07 and 02.02.08) that are listed in the WET data base. The waste stream numbers are designed to classify the streams by various physical and chemical properties. As Table 3-5 illustrates, the WET Model categorizes according to waste type and waste properties. More specifically, waste type is classified as the source of the waste, e.g., light ends from glycerin production using alkyl chloride. As suggested earlier, a listing of waste streams by process source greatly facilitates waste-specific identification. The waste properties listed by the WET Model include waste biodegradation rate, biological oxygen demand, and pH. More importantly, however, the WET Model lists the hazardous constituents of concern along with their vapor pressures. This allows a relatively simple assessment of the hazardous volatile constituents of the streams. The WET Model also lists potentially applicable treatment technologies for each waste stream, along with an estimated waste generation rate per facility.

While the WET Model provides a great deal of information that would be useful in assessing potential pretreatment technologies, it does have several inherent inadequacies that should not be overlooked. First, the data compilation was intended primarily to characterize wastes considered hazardous or potentially hazardous under Subtitle C of RCRA (US EPA 1983b). Consequently, the WET data base does not characterize the "universe" of hazardous waste streams. EPA-OSW studies aimed at defining a wider range of hazardous waste streams are in progress, however. This will be a continuing process. Second, it must be remembered that there is an inherent difficulty in trying to characterize the waste generated by a single type of industrial process. The complexities and variations in process parameters at different plants within a given industry make the task of defining the "typical" waste a difficult one. For this reason, there is inherent uncertainty in the WET Model where waste stream characteristics, particularly

TABLE 3-5. WASTE STREAM LISTING FROM THE WET MODEL HAZARDOUS WASTE DATA BASE[a]

```
 WASTE STREAM
 NUMBER / NAME                                                                                   EPA NUMBER(S)
 -------------                                                                                   -------------

02.02.07 / LIGHT ENDS FROM GLYCERIN PRODUCTION FROM ALLYL CHLORIDE                                    N/A

 QUANTITY PER   FRACTION  FRACTION   SOLIDS  AVG.  HEATING      FRACTION FRACTION      BIODEGRADATION      BOD(T)
FACILITY(KG/DAY) NONWATER SUSPENDED   S.G.   S.G. VALUE(KJ/KG)    CL       ASH     PH  RATE (PER DAY)      (MG/L)
   ---------    --------  ---------  ------  ---- ------------  ------   ------   ---- --------------      ------
    2,900.0       .080      .020      1.50   1.00   2,500.0       .00      .02     .0        .00              .00

    CONSTITUENT                MASS    FRACTION  MOLECULAR     VAPOR        SOLUBILITY  BIODEGRADATION     BOD
    OF CONCERN               FRACTION  DISSOLVED   WEIGHT   PRESSURE(TORR)  (MG/L)@ 25C. RATE(PER DAY)   ULTIMATE
    -----------              --------  ---------  --------- --------------  ----------- ------------   ------------
    TOLUENE                  .050000    1.000        92.0      28.70        534.8        2.690          2.640

    APPLICABLE TREATMENT TECHNOLOGIES
    ---------------------------------
    NO TREATMENT
    AEROBIC BIOLOGICAL TMNT
    INCINERATION

 WASTE STREAM
 NUMBER / NAME                                                                                   EPA NUMBER(S)
 -------------                                                                                   -------------

02.02.08 / VENT SCRUBBER EFFLUENT FROM MALEIC ANHYDRIDE PROD BY BENZENE OXIDATION                     N/A

 QUANTITY PER   FRACTION  FRACTION   SOLIDS  AVG.  HEATING      FRACTION FRACTION      BIODEGRADATION      BOD(T)
FACILITY(KG/DAY) NONWATER SUSPENDED   S.G.   S.G. VALUE(KJ/KG)    CL       ASH     PH  RATE (PER DAY)      (MG/L)
   ---------    --------  ---------  ------  ---- ------------  ------   ------   ---- --------------      ------
    31,100.0      .169      .020      1.50   1.00   6,800.0       .00      .02     .0        .00              .00

    CONSTITUENT                MASS    FRACTION  MOLECULAR     VAPOR        SOLUBILITY  BIODEGRADATION     BOD
    OF CONCERN               FRACTION  DISSOLVED   WEIGHT   PRESSURE(TORR)  (MG/L)@ 25C. RATE(PER DAY)   ULTIMATE
    -----------              --------  ---------  --------- --------------  ----------- ------------   ------------
    BENZENE                  .167000    1.000        78.0      95.20        1780.        2,460          1,980
    MALEIC ANHYDRIDE         .001000    1.000        98.0      .1000        .1630E+06    .5000E-01      .0000E+00

    APPLICABLE TREATMENT TECHNOLOGIES
    ---------------------------------
    NO TREATMENT
    INCINERATION
    STRIPPING-AIR
    AEROBIC BIOLOGICAL TMNT
    ION EXCHANGE
```

---

[a] Source: US EPA (1983b). Physical properties are for the pure compound at 25° C.

of industrial process. The complexities and variations in process parameters at different plants within a given industry make the task of defining the "typical" waste a difficult one. For this reason, there is inherent uncertainty in the WET Model where waste stream characteristics, particularly stream composition, are conerned. Production facilities also vary a great deal in terms of production rate; consequently, the waste generation rate (per facility) data from the WET Model are also subject to uncertainty. The WET Model does address uncertainties in waste composition (constituent concentration) and estimated waste generation rates (quantity generated per facility), however. This is accomplished by associating an "uncertainty factor" with these types of estimates (US EPA 1983b). This should allow users of the data to estimate the error that might result when WET data are taken to be representative of domestic industry as a whole. It should also be noted that the lists of applicable treatment technologies contained in the WET Model are not based entirely on demonstrated applications. In many cases, treatment technologies were matched with waste streams based upon engineering judgment only. In addition, the hazardous constituents of concern listed in the WET Model do not necessarily include all of the volatile species in each listed waste stream.

Finally, it should be noted that the WET Model iteself is being updated by EPA's Office of Solid Waste. As of May 1984, the data base contained 257 waste streams (not all RCRA hazardous wastes) totalling 160 million metric tons per year. This updating included some revisions to data contained in the 1983 WET Model data base used in this study. Because of limited funds and the complexities of revising an extensive data base, it was decided not to revise the analyses that had already been performed in this report. As a result, the reader is cautioned that while the qualitative results obtained in this report using the WET Model data base and the methodology for obtaining them should be valid (and appropriate for a preliminary engineering assessment), quantitative results (e.g., waste stream emissions) should be used with caution.

3.2.3 Assessment of Air Emissions From Hazardous Waste TSDFs (Hazardous Waste Ranking, GCA Model)

This work resulted in a hazardous waste prioritization designed to provide an estimate of the potential inhalation health impact of hazardous wastes currently being disposed of in the United States (US EPA 1983c). The primary objective of this waste prioritization was to identify a select group of hazardous wastes for subsequent analysis of air emissions under other EPA projects.

Waste characterization data and chemical property data were required for input to the hazardous waste ranking. The goal was to rank the emissions risk potential for all selected chemicals based upon their presence in both the chemical-specific (U and P) waste codes, and the generic (K, D, and F) waste codes. Waste streams were also prioritized based on the volatility and health hazard of all volatile constituents in each waste stream. Pertinent data from several EPA programs were collected and compiled. Waste characterization data were compiled for 47 generic waste codes and 54 chemical-specific codes. Waste generation data, i.e., volume generated per year, were weighted by toxicity data to provide waste rankings.

The GCA model, by design, is best suited for use in work relatd to risk analysis. Consequently, it has limited utility insofar as providing data that can be used for matching hazardous waste streams with candidate pretreatment technologies. This is largely due to the fact that there is insufficient information about waste stream characteristics, beyond their volatile constituent content. The GCA model waste rankings do, however, provide a numerical comparison of the potential air emissions hazard posed by various wastes. Thus, information from the GCA model might be used as a tool for selecting waste streams to be considered for pretreatment.

At this point, it should be noted that some of the major chemical species listed in the GCA model are not accounted for in the WET model, indicating that the WET model is incomplete. Since the GCA model rankings are based upon toxicity weighted waste generation data, large volume sources may be deleted if their toxicity as judged by GCA methodology is not significant.

3.2.4 Survey of Potential Hazardous Waste Streams (Industrial Organic Chemicals Manufacturing Industry)

This survey was conducted to assess potential hazardous waste generation from 147 various organic chemical related processes. Upon conclusion, 542 waste streams were identified (US EPA 1982). The Industrial Organic Chemicals Manufacturing Industry (IOCMI) survey includes data describing the type and number of waste sources within a given process, the quantity of waste generated per unit time, and the chemical composition of the waste stream. Thus, the reduced data consist of waste type and property listings. The IOCMI survey also rank orders the identified streams in three ways:

- By total mass (Mg/yr) of the stream generated
- By total mass (Mg/yr) of nonaqueous waste generated
- By total mass (Mg/yr) of hazardous constituents in the stream.

As one would anticipate, data abstracted from the IOCMI survey will have some degree of uncertainty associated with it. The survey contractor (IT-Enviroscience) noted the wide disparity in quality among the various data that compose the survey (US EPA 1982). The data used to determine the production or capacity of a specific chemical process were of better quality than the data related to the total quantity of waste generated from a process. Similarly, the data related to the total quantity of waste generated were of better quality than the data describing waste stream compositions. While the survey does not quantitatively assess the error associated with various data, data sources are noted in some cases, e.g., published data or engineering estimate. Information in this data base was used to check WET model data for streams that were common to both.

3.3 SUMMARY

Comparing data from the OSW-TSDF National Survey, the WET Model*, the GCA Model, and the IOCMI Survey, it is evident that the WET data base will be the easiest to use as far as pretreatment assessment is concerned. This is true for the following reasons:

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*As noted in the Introduction, the WET Model is being updated and some of the Model data used in this report may change. Note also that the WET Model data base is more recently being referred to by EPA as the "Waste Stream Data Base" of the RCRA Risk-Cost Analysis Model.

- Waste Stream volatility is more easily evaluated.
- The compatibility of a waste stream with a specific pretreatment technology can be assessed using the stream composition data.
- Equipment scale can be estimated from the "quantity generated per facility" data. Pretreatment examples (Section 5) are based on this scale. This implies, in most cases, that the equipment scale is smaller than for a central TSDF treating wastes from many sources. However, this choice is made because it is difficult to define an alternative scale (e.g., the size of a centralized TSDF would be completely arbritrary).

Section 5 summarizes the approach used to assess pretreatment options for waste streams that contain volatile constituents.

The shortcomings associated with relying on the WET data base should be recognized. First, the WET Model was intended primarily to characterize wastes containing hazardous constituents (as specified under Subtitle C of RCRA); therefore, it is possible some volatile-containing streams may be overlooked. In addition, there is inherent uncertainty in the stream composition data provided by the WET Model--primarily because of process variations at the various waste generators. Finally, the waste generation rate data must be used in estimating pretreatment system scale. The range of this parameter may be quite large, and economic evaluations based upon only one pretreatment equipment scale may be misleading because of potential economies of scale.

SECTION 4

TREATMENT, STORAGE, AND DISPOSAL FACILITY (TSDF) CHARACTERIZATION

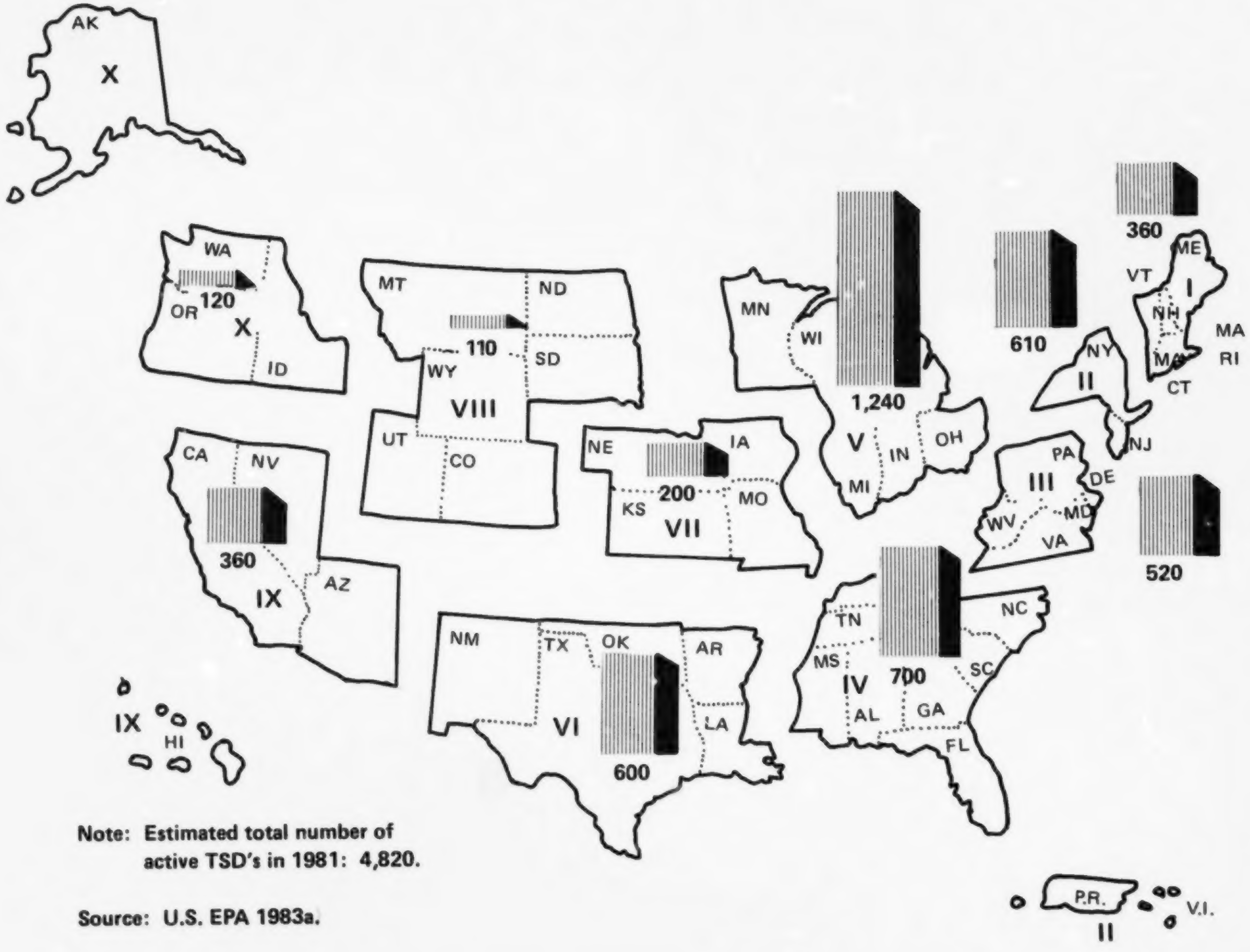
The purpose of Section 4 is to summarize the available information on the characteristics and physical size of TSDFs in order to gain a perspective on the problem of volatile emissions from various TSDF operations.

4.1 THE DOMESTIC TSDF POPULATION

Figure 4-1 presents the regional distribution of TSDFs as predicted from the Office of Solid Waste (OSW) TSDF National Survey (US EPA 1983a). As indicated, the total number of TSDFs (during 1981) was estimated to be 4,820. The majority of the domestic TSDFs are believed to be located in EPA Region V, which accounts for 1,240, or approximately 25.7 percent, of the estimated 4,820 facilities. As noted, Puerto Rico (Region II), Hawaii (Region IX), and Alaska (Region X) are estimated to have no TSDFs.

Figure 4-2 illustrates the number of commercial versus other types of TSDFs as predicted from preliminary results of the OSW TSDF National Survey. As shown, preliminary estimates indicate that about 4,450 of the 4,820 domestic TSDFs, or 92 percent of the population, handle waste generated primarily in-house (50 percent or less of the total waste processed comes from other firms). This confirms the general observation that the overwhelming majority of hazardous waste is managed onsite. Preliminary estimates from the same survey indicate that, of the 40 billion gallons of hazardous waste generated in 1981, 38 billion gallons (95 percent) were managed onsite.

Figure 4-3 illustrates domestic TSDF capabilities as predicted from the OSW survey. As indicated, most of the domestic TSDFs (4,300) practice waste storage in addition to any other treatment and/or disposal practices. Thus, about 89.2 percent of the domestic TSDFs are capable of storing hazardous wastes. It has also been estimated that about 1,500 TSDFs, or


AK
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WV
MD
VA
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P.R.
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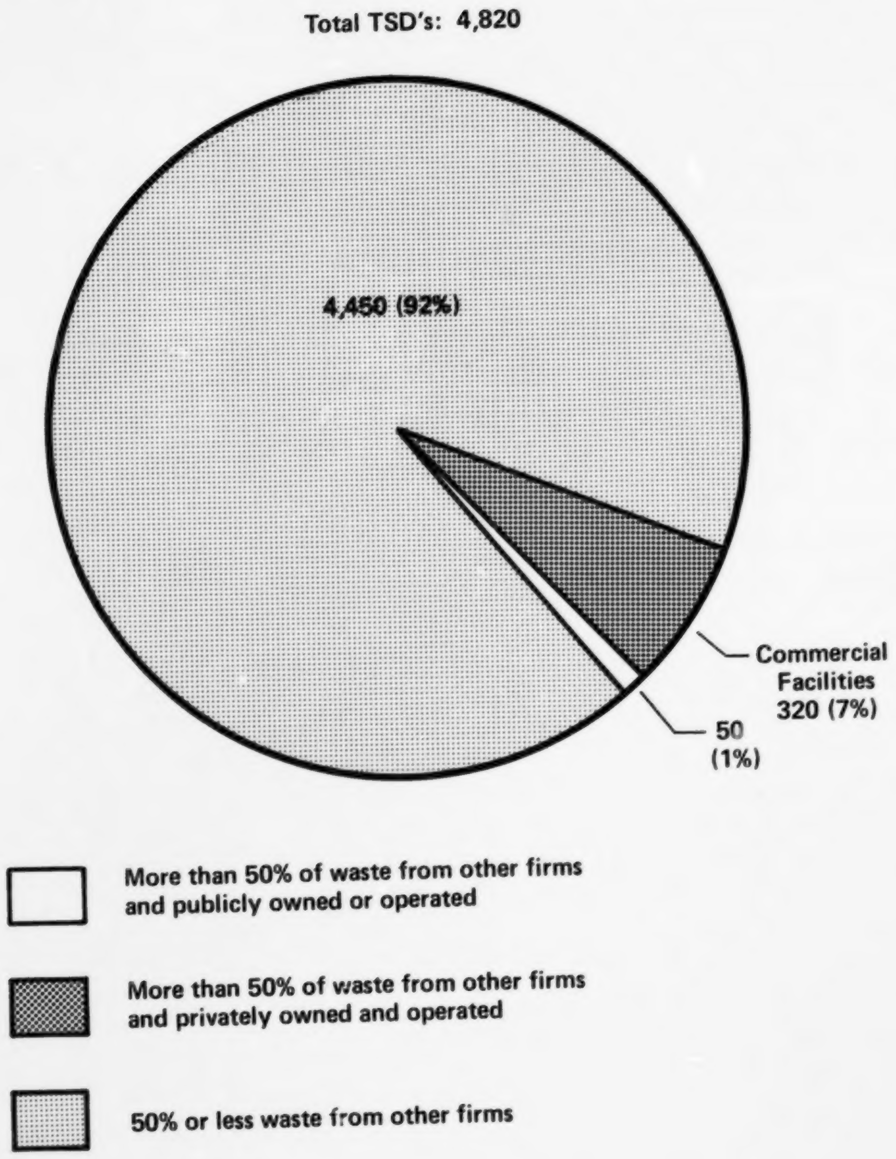
II

Note: Estimated total number of active TSD's in 1981: 4,820.

Source: U.S. EPA 1983a.

Figure 4-1. Regional distribution of treatment, storage, disposal facilities in 1981.



Source: U.S. EPA 1983a

Figure 4-2. Number of commercial versus other TSD facilities.

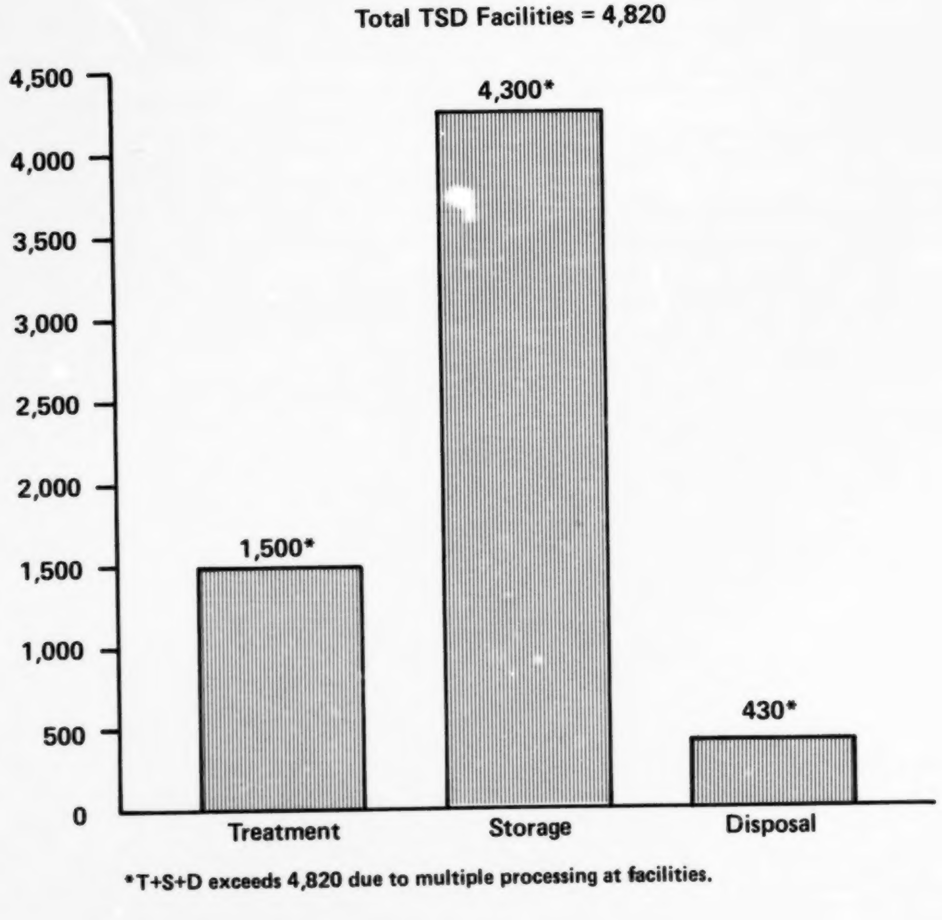


Figure 4-3. Number of facilities with treatment, storage, and/or disposal in 1981.

31.1 percent of the population, conduct hazardous waste treatment in addition to any other storage and/or disposal activities. Similarly, it is estimated that only 430, or 8.9 percent, of the 4,820 domestic TSDFs conduct waste disposal operations.

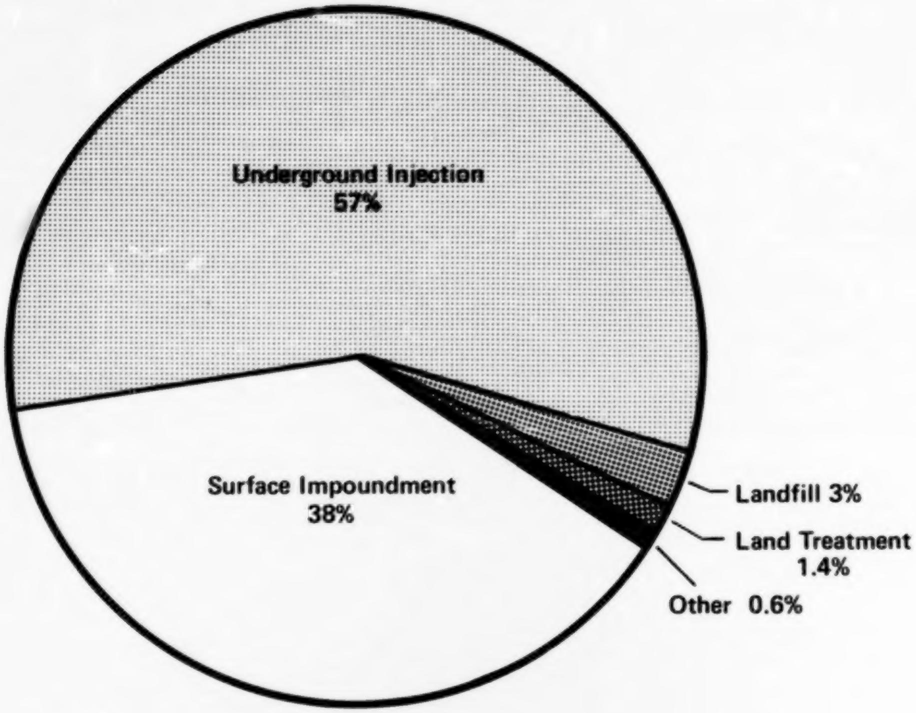
4.2 TREATMENT, STORAGE, AND DISPOSAL PRACTICES

Preliminary data from the OSW TSDF National Survey have been used to estimate the number of facilities using selected treatment, storage, and disposal processes. The resulting estimates are presented in Table 4-1. While a breakdown of process type by quantity of waste handled might be more informative, the preliminary data does not allow the preparation of such estimates for storage and treatment processes. However, for several disposal technologies such a breakdown is available, and these estimates are presented in Figure 4-4. It is estimated that most hazardous waste disposal in 1981 used underground injection. From the standpoint of air emissions, this is favorable since emissions associated with this technique are judged to be minuscule. The estimates indicate that during 1981 approximately 8.9 million gallons of hazardous waste was disposed of using underground injection. This quantity constitutes about 57 percent of the total hazardous waste disposal for that year (15.6 billion gallons). Surface impoundment was the second most common means of waste disposal, accounting for about 38 percent, or 5.9 million gallons, of the total waste disposed. Landfill, land treatment, and other disposal techniques represent the remaining 5 percent, accounting for about 0.8 million gallons of waste.

TABLE 4-1. NUMBER OF FACILITIES USING SELECTED TREATMENT, STORAGE, AND DISPOSAL PROCESSES

Process type	Number of facilities in 1981[a]
Storage container	3,580
Storage tank	1,430
Surface impoundment	770
Treatment tank	610
Incinerator	240
Landfill	200
Waste pile	170
Injection wells	90
Land treatment	70
Other processes	320
Total TSDFs: 4,820[a]	

[a] Sum of process types exceeds 4,820 due to multiple processing at facilities.



Total Quantity Disposed:
15.6 Billion gallons (58 million metric tonnes)

Source: U.S. EPA 1983a

Figure 4-4. Quantities of hazardous waste disposed in 1981.

SECTION 5

PRETREATMENT TECHNIQUES

This section discusses the techniques available for pretreating hazardous wastes to remove volatile organic components. First, the general approach to evaluating candidate treatment techniques is described. Then, each technique is evaluated in detail, providing a brief description of the technique, the status of its commercial development and advantages and disadvantages of its use. An example application is provided to obtain an estimate of treatment costs and further research is recommended.

Initially, RTI evaluated all waste treatment technologies to determine their potential for pretreating volatile waste streams. The results of this evaluation are summarized in Table 5-1. The technologies judged to be the most applicable are the following:

- steam stripping
- chemical oxidation
- carbon adsorption
- resin adsorption
- evaporation/adsorption
- air stripping/adsorption
- biological treatment
- ozonation/radiolysis
- distillation
- wet oxidation
- solvent extraction
- physical separations

These 12 technologies are evaluated in detail in this section. Each of these technologies is matched with appropriate waste streams contained in the WET Model data base. This was accomplished using engineering judgement based upon the physical and chemical nature of the streams as described in the WET data base.

TABLE 5-1. TECHNOLOGIES EVALUATED AS POTENTIAL PRETREATMENT OPTIONS*

Unit operation	Applicability for the pretreatment of volatile hazardous waste streams		
	Applicable	Possibly/potentially applicable	Not applicable
Carbon adsorption	Capable of removing a large variety of organic solutes from aqueous streams.		
Resin adsorption	Capable of removing organic solutes from organic waste streams. Preferred when the absorbate is to be recovered.		
Biological treatment			
· activated sludge	Probably the most cost-effective method of destroying organics present in an aqueous waste stream.		
· aereated lagoons		Does decompose organics. Not very attractive for wastes with highly variable organic concentrations.	
· anaerobic digestion		Used mostly for the decomposition of solids, e.g., sewage sludges.	
· composting		Can be used most easily with solid wastes.	
· enzyme treatment			Enzymes cannot adapt to the varying compositions of typical waste streams.
· trickling filters	Proven technology for the decomposition of organics in waste streams with less than 1% concentration		

(continued)

TABLE 5-1 (continued)

Unit operation	Applicability for the pretreatment of volatile hazardous waste streams		
	Applicable	Possibly/potentially applicable	Not applicable
Centrifugation			Liquid/solids separation process.
Dialysis			Output streams not likely to be any more amenable to disposal than input streams.
Dissolution			Involves removing constituents from solids.
Distillation	Well-established unit operation for separating compounds based upon differences in volatility.		
Electrodialysis			Not demonstrated. Never employed on a full scale.
Electrolysis			Not generally useful for organic waste streams.
Electrophoresis			No suitable equipment available.
Evaporation	Well-established process for the removal/reclaimation of volatile species.		
Filtration			Liquid/solids-gas/solids separation process.

(continued)

TABLE 5-1 (continued)

Unit operation	Applicability for the pretreatment of volatile hazardous waste streams		
	Applicable	Possibly/potentially applicable	Not applicable
Flocculation, precipitation, and sedimentation			Most suitable for removal of soluble heavy metals and solid particles.
Floatation			Solid/liquid separation process.
Freeze crystallization		Might be used to concentrate waste streams prior to treatment.	
Freeze drying			Slow, costly, and energy intensive
Freezing, suspension			Primarily for sludges
High gradient magnetic separation			Not well developed for liquid-liquid separation.
Hydrolysis		Possible use in decomposing organics. Not well demonstrated for waste treatment.	
Ion exchange			More suitable for the recovery of heavy metals.
Liquid ion exchange			More suitable for the recovery of heavy metals.
Microwave discharge			Still in the development stage.

(continued)

TABLE 5-1 (continued)

Unit operation	Applicability for the pretreatment of volatile hazardous waste streams		
	Applicable	Possibly/potentially applicable	Not applicable
Neutralization		Might be used as a precursor to stream treatment in some cases.	
Oxidation, chemical	Medium-scale applications are well established for the degradation of aqueous organics and inorganics.		
Oxidation, wet	Well demonstrated technology for treating commercial wastes.		
Ozonation/radiolysis	Technology is well developed for degradation of cyanides and phenols. Pilot studies indicate potential for treatment of chlorinated hydrocarbons, polynuclear aromatics, and pesticides.		
Photolysis		Not highly developed for large-scale application. Capable of partial degradation of organics.	
Reverse osmosis		Not well demonstrated (large-scale) for recovering organics from waste streams.	
Stripping, air	While not well demonstrated for this purpose, should be capable of recovering volatile constituents from some waste streams.		

(continued)

TABLE 5-1 (continued)

Unit operation	Applicability for the pretreatment of volatile hazardous waste streams		
	Applicable	Possibly/potentially applicable	Not applicable
Stripping, steam	Proven process for removing volatile compounds from waste streams.		
Ultrafiltration		Most useful for separation of high molecular weight compounds from surrounding media.	
Zone refining			Not suitable for handling large quantities.

*This table only considers the technical applicability of a treatment process toward removing volatile organics from waste streams. In determining applicability it does not consider the need for or difficulties associated with properly disposing of treatment process residuals. Such considerations are addressed in Section 5.

the streams as described in the WET data base. The results of matching all WET Model streams with the 12 pretreatment techniques are presented in Section 6.

It is important to note that in actual practice, well-defined hazardous waste streams of constant composition may exist only at the point of generation, and perhaps not even there as a general rule. Thus, the matching of pretreatment techniques with any listing of specific volatile-containing hazardous waste streams is somewhat artificial. In actual practice, the owner/operator of a TSDF will deal with a mixture of numerous streams whose composition and chemical/physical properties change with time. However, a matching of pretreatment techniques to specific waste streams allows at least a preliminary assessment of applicable techniques for volatile removal knowing either the source or generic characteristics of the waste stream. Table 5-1 summarizes the generic characteristics of various waste streams and applicable pretreatment techniques.

In choosing the most widely applicable pretreatment techniques to be carbon adsorption (liquid and gas phase), steam stripping, and batch distillation, great weight was given to the variety of wastes that would be treated at a TSDF and whether these techniques are suitable to remove volatile constituents from sludges, aqueous liquids, organic liquids, solids-containing liquids, etc. These pretreatment techniques, perhaps in various combinations, would serve to treat most of the waste streams with significant volatile content that would be received, based on information in the WET Model.

Once the streams judged to contain volatile constituents are matched with candidate pretreatment technologies, the WET data or waste generation rate (quantity generated per facility) can be used as the basis for determining the appropriate equipment scale.[1] Material balances and equipment cost estimates based on this scale are then used to estimate economic parameters, i.e., cost and cost-effectiveness, associated with each technology as given in Appendix A. Example assessments are presented in subsequent sections for all of the candidate pretreatment technologies listed above. The IOCMI survey and other data sources (see Section 3) such as EPA hazardous waste stream data were used, when possible, to supplement the data obtained from the WET data base.

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[1] Some of the waste generation rate data from the WET Model appear to be suspect because the generation rates are unusually small. Thus, when choosing a basis for equipment scale, these data should be used with discretion. The WET Model is currently being updated by EPA.

The shortcomings associated with relying on the WET data base are enumerated in Section 3. As mentioned there, the streams contained in the WET data base probably do not represent the "universe" of hazardous waste streams. As such, some significant volatile streams could be overlooked. One must also recognize the potential shortcomings of using a waste generation per facility data contained in the WET Model as the basis for equipment sizing. There are two reasons for this. First, the range associated with this parameter may be quite large. Secondly, several waste streams may be mixed together prior to pretreatment, particularly if pretreatment is occurring at a commercial TSDF. This will require a larger treatment unit. Consequently pretreatment economics based upon only one equipment scale may be somewhat misleading in that potential economics of scale may be overlooked. In the absence of a better method, the cost (either capital cost or total annualized cost) of a given pretreatment technique can be assumed to vary with the quantity of material processed raised to the 0.6 power. The general concept of using waste generation data to estimate equipment scale appears to be sound, however. This judgment is based upon preliminary results of the OSW-TSDF National Survey which indicate that the majority of the hazardous waste generated is treated onsite. It is estimated that, in 1981, 95 percent of the hazardous waste generated (~ 144 billion liters) was managed onsite (U.S. EPA 1983a).

The cost of a pretreatment process depends on many factors, including:

- Volatile content of the waste stream (kg volatile/kg waste stream treated)
- Required volatile removal efficiency (kg volatile removed/kg waste stream treated)
- Size (kg waste stream treated)
- Design constraints (e.g., limits on emissions or energy consumption for the pretreatment process itself)
- Raw material and labor cost

For each pretreatment technique discussed in the balance of Section 5, an example case (i.e., a specific WET Model stream) has been selected and costs prepared for the application of a specific technique (e.g., steam stripping) to a specific WET Model stream (e.g., stream 02.02.14, bottoms from an ethylene cracking unit). Specific details of the capital cost, annual operating cost, and total annualized cost for each example case are given in the discussion of individual pretreatment techniques. These costs consist of the following:

- Capital cost: purchased equipment, design and engineering, startup, and contingency
- Annual operating cost: operation and maintenance labor and materials, utilities, and cost of disposal of residues from the pretreatment process itself, if applicable.
- Total annualized cost: sum of the annual operating cost and capital recovery cost, based on typical book life of equipment of 10 percent per year. The capital recovery cost is thus 16.265% of the capital cost.

The cost of each pretreatment technique case includes the cost environmentally safe residue disposal, if needed. Also included are any byproduct recovery credits (e.g., for relatively pure solvents that may be recovered in batch distillation).

5.1 STEAM STRIPPING

5.1.1 Introduction

Steam stripping is a commercially proven process that is commonly used to remove volatile compounds from aqueous process effluents such as wastewater streams. The process essentially involves fractional distillation of volatile constituents from an aqueous stream. In most instances, the volatile species is water soluble. More recently however, stream stripping has been used to recover species that exhibit limited miscibility in water, e.g., chlorinated hydrocarbons. The product streams from the process are typically a concentrated vapor or liquid solution containing most of the volatile species, and a very dilute treated aqueous stream containing small amounts of dissolved gases or volatile species.

5.1.2 State of the Art

The equipment required for steam stripping is nearly identical to that required for distillation. These required items of equipment include a packed or tray column, a reflux condenser/splitter, and appropriate feed tanks and pumps. A typical steam stripping system is illustrated in Figure 5-1.

Steam stripping is usually conducted as a continuous operation (Berkowitz et al. 1978). The preheated feed stream is introduced near the top of the column and then flows (by gravity) countercurrent to the steam and organic vapors that rise to the top of the column. Steam is introduced at the bottom of the column as shown in Figure 5-1. As the liquid phase flows downward through the column, it becomes progressively leaner in volatile matter. Similarly, the gas phase becomes richer in volatile matter as it flows up through the column. The overhead vapor is condensed as it exits the column, and the condensate is then usually routed to a decanter where the aqueous phase (mostly water) is removed and returned to the column. Because the solubility of volatile constituents is less at the condensate temperature, most of the volatiles are removed by phase separation. Reflux may or may not be used, depending upon the desired composition of the overhead stream. As illustrated, the stripped liquid exiting the bottom of the column is typically used to heat the feed via indirect heat exchange.

The efficiency of steam stripper recovery is dependent upon numerous variables. The most important of these are as follows:

- Number of stages provided for vapor-liquid contact
- Steam input rate
- Temperature of operation (condition of input steam)
- pH of the liquid phase

The area available for intimate vapor-liquid contact is directly proportional to the number of stages (or number of gas-phase transfer units in the case of a packed colunn) provided. The steam input rate and condition (i.e., temperature, pressure, and thus enthalpy) will determine the vapor velocity and temperature distribution within the column. The temperature within the column is of paramount importance since temperature markedly affects the solubility of the volatile species in water. Liquid pH has also been observed to affect solubility (Berkowitz et al. 1978).

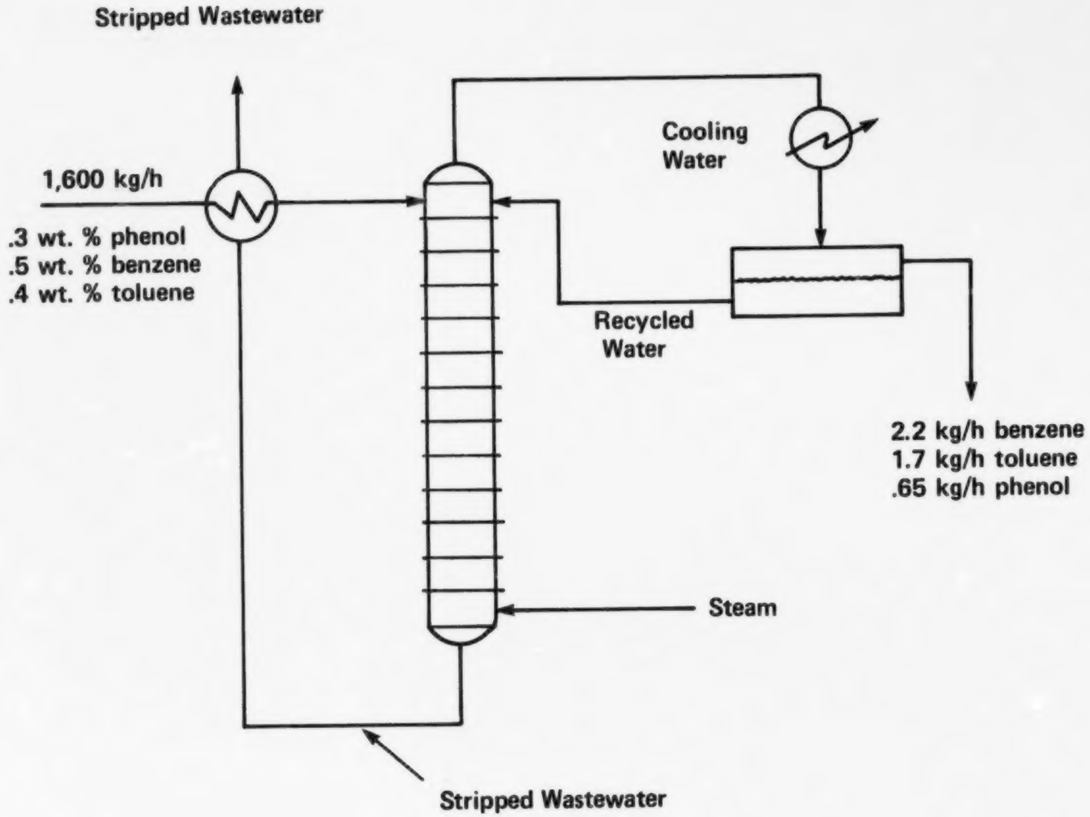

Stripped Wastewater
1,600 kg/h
.3 wt. % phenol
.5 wt. % benzene
.4 wt. % toluene
Cooling Water
Recycled Water
2.2 kg/h benzene
1.7 kg/h toluene
.65 kg/h phenol
Steam
Stripped Wastewater

Figure 5-1. Process flow sheet and mass balance for steam stripping pretreatment of WET stream 02.02.14.

5.1.2.1 Status of Commercial Development--

Steam stripping is currently used in both industrial chemical production (for product recovery and separation) and in industrial waste treatment. Several demonstrated examples of product recovery by steam stripping are the following:

- Ammonia recovery (for sale as ammonia or ammonium sulfate) from coke oven gas-scrubber water
- Sulfur recovery from refinery sour water
- Phenol recovery from aqueous solutions generated in the production of phenol

More recent applications have involved the use of steam stripping for recovering organics from wastewater. Some of these applications involve the removal of phenols, mercaptans, and chlorinated hydrocarbons from wastewaters.

Dow Chemical's Midland, Michigan, plant contains a steam stripping section that reduces wastewater phenol content to 150-750 ppm (Berkowitz et al. 1978). This stream is subsequently treated by carbon adsorption. B.F. Goodrich has announced the development of a continuous steam stripping system for removing vinyl chloride monomer from suspension resins of polyvinyl chloride. In addition, Kraft mill condensates are steam stripped to remove methanol and sulfur compounds at a pulp and paper mill owned by the Mead Corporation (Berkowitz et al. 1978). The performance of this system is illustrated in Table 5-2. This system handles about 200 gal/min of Kraft mill condensate and requires about 10,000 lb/h of steam.

EPA's Robert S. Kerr Environmental Research Laboratory has studied the removal of low molecular weight chlorinated hydrocarbons from process wastewater by steam stripping (Berkowitz et al. 1978). For waste streams containing 3000-6000 ppm chlorinated hydrocarbon removal efficiencies of up to 90 percent have been obtained.

5.1.2.2 Constraints and Restructions--

Since steam stripping is basically a form of fractional distillation, many of the same restrictions apply (see Section 5.6). The feed must be a free flowing liquid with negligible solids content (Perry and Chilton 1973). As with distillation, solids will tend to foul and plug the column

TABLE 5-2. PERFORMANCE DATA FOR STEAM STRIPPING OF KRAFT MILL CONDENSATES[a]

Component	Concentration	
	Before stripping	After stripping
BOD	10,000 ppm	2,500 ppm
Methanol	0.8 vol percent	0.2 vol percent
Total reducible sulfur	20,000 ppm	100-200 ppm

[a] Source: Berkowitz et al. 1978.

internals. Thus, if the solids content is appreciable, some form of solids removal will be required. It is also quite likely that steam strippers may not adapt to changes in feed composition while still maintaining the desired separation. Consequently, it would be desirable to have a steady supply of feed with a relatively constant composition.

5.1.3 Example Case

Preliminary capital and operating cost estimates have been developed for a continuous steam stripping unit designed to treat 17,750 kg/h of benzene, toluene, and phenol contaminated solution generated from the bottoms of an ethylene cracking unit. This feed stock corresponds to stream 02.02.14 of the WET Model Data Base. The design basis is as follows:

- Feed rate of 17,750 kg/h wastewater (roughly .3 weight percent phenol, .4 weight percent toluene, and .5 weight percent benzene by weight)
- Column operation at atmospheric pressure
- Isothermal operation at about 100° C

It was determined by engineering estimate that a bubble cap tower with 12 stages would be adequate to effect the desired separation. Column diameter was estimated to be 3 meters. This system is illustrated in Figure 5-1.

Assuming operation for 350 days per year (@ 24 h/day), organics would be recovered at the rate of about 1,535 Mg/yr. It has been assumed that this product can be recycled or sold at cost to offset any disposal costs (disposal costs for products that cannot be recycled vary greatly depending on their heat value and toxicity; the principal means of disposal for most volatile wastes is incineration.)

The total capital cost for this scenario (including direct, indirect, and contingency costs) was estimated to be about $1,278,660 (January 1983 dollars). Discounting the capital cost at 10 percent over 10 years results in a total annualized cost of $4,026,000/yr. The unit cost is estimated to be $0.026/kg of waste treated.

5.1.4 Advantages and Disadvantages

The primary advantages associated with steam stripping are the following:

- Steam stripping is well-established on a commercial scale, thus there are few uncertainties regarding its performance.
- Steam stripping is capable of recovering (rather than destroying) volatile species.
- A steam stripping unit is capable of handling a variety of volatile constituents in liquid waste streams, provided the liquids are relatively insoluble in water.

Techniques for designing and predicting the performance of strippers are well established in the chemical engineering literature (e.g., McCabe and Smith 1976). In addition, commercial-scale applications such as those mentioned previously have demonstrated the capability of steam stripping for recovering volatile constituents from aqueous streams.

Steam stripping, like distillation, is also capable of recovering volatiles in a concentrated form without chemical degradation of the species involved. This ability would tend to make steam stripping attractive in cases where the recovered volatiles might be recycled or sold.

The primary disadvantage of steam stripping is its tendency to be energy-intensive and thus expensive. The cost associated with steam is typically much larger than other annual costs (including capital recovery). This is evidenced by the costs presented above.

5.1.5 Recommendations for Further Study

Steam stripping is a proven process that is capable of removing volatile compounds from many types of liquid effluents including aqueous process or wastewater. Sufficient data currently exist for the design of steam strippers for many applications involving the reclaimation of volatile constituents.

It is likely that with wastewater guidelines becoming more stringent, steam stripping of wastewater will become more widespread (Berkowitz et al. 1978). Such technology is well developed for cases where the volatile constituent is appreciably soluble in water. Technology for removing water-immiscible organic compounds from aqueous streams via steam stripping is not well developed however. Consequently, further research into this area may be warranted.

5.2 CHEMICAL OXIDATION

5.2.1 Introduction

Chemical oxidation for pretreatment of hazardous wastes involves the addition of an oxidizing agent to the waste to destroy volatile species or to convert them into less volatile species through partial oxidation. The process is primarily applicable to aqueous organics, (e.g., phenols or amines) and aqueous inorganics (e.g., sulfide or cyanide). Previous oxidizing agents have included ozone, hydrogen peroxide, potassium permanganate, and chlorine and its derivatives (sodium hypochlorite and chlorine dioxide). Air and oxygen can also be used but where the goal is pretreatment to prevent emissions of volatile chemicals, these oxidants are not likely to be adequate. Volatile chemicals that would react rapidly and completely with air are unlikely to present emissions problems.

5.2.2 State of the Art

5.2.2.1 General Process Description--

5.2.2.1.1 Hydrogen Peroxide--Hydrogen peroxide has been used in numerous cases to maintain oxidizing conditions in various municipal sewage treatment operations. Industrial waste applications include the oxidation of sulfide to sulfate in refinery wastes (Shepard 1977) and tannery wastes (O'Neal et al. 1977). Phenolic waste streams from pharmaceutical manufacturing, tin plating, and paint stripping have been treated with hydrogen peroxide on a commercial basis (Sims 1981).

Laboratory and bench-scale testing has confirmed the technical feasibility of hydrogen peroxide treatment of wastes containing aldehydes, cyanide, hydroquinone, and reduced sulfur compounds. These compounds may be present in waste streams from electroplating, timber, textiles, pigment, chemicals, pulp and paper, refining, and iron and steel industries (FMC Corp).

Processing equipment is conceptually simple as shown in Figure 5-2. Hydrogen peroxide, available as bulk liquid in either 50 or 70 percent weight solutions (in water), is metered into the waste stream and given sufficient reaction time. Residence times are typically on the order of 30 minutes. In some cases, the rate of reaction can be increased by adjusting pH.

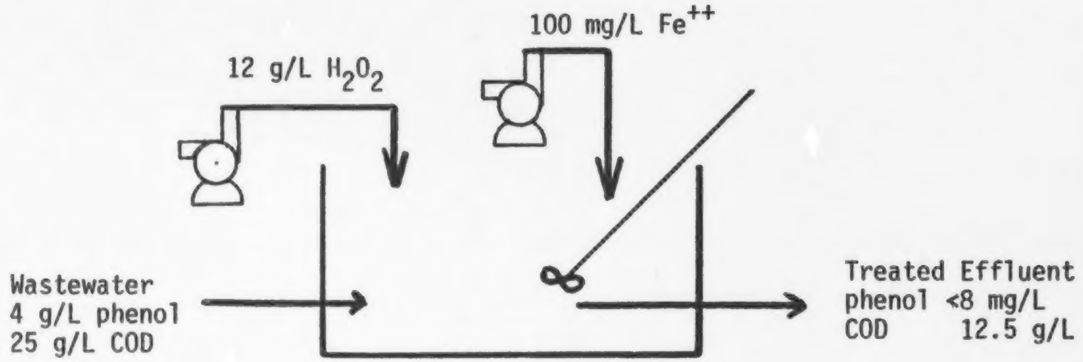
Hydrogen peroxide treatment takes place when hydrogen peroxide contacts the wastewater either in a separate holding tank or in a pipeline connecting two vessels. If emissions from a holding tank require control, some emission reductions may be achieved by adding hydrogen peroxide directly to the holding tank.

Although most applications of hydrogen peroxide addition occur in sewage treatment (including aerobic biological treatment of industrial wastes), the process is used in specific industrial applications. The technology has been applied on a regular basis to waste treatment systems, but it is often considered a high operating/low capital cost solution for intermittent, emergency, or as needed use. A flow sheet for hydrogen peroxide treatment of paint stripping effluent is given in Figure 5-2. In this case, ferrous ion is used as a homogenous oxidation catalyst.

The advantage of hydrogen peroxide treatment is its relatively low capital cost and land requirement In addition, it creates no sludges or concentrated waste streams and is extremely flexible in terms of "turn down" for varying flow rates or concentrations. Hydrogen peroxide addition rates can be varied depending on waste stream volume and composition. Disadvantages include high operating cost due to the cost of the hydrogen peroxide (approximately $0.60/lb in bulk), potentially hazardous incomplete oxidation products, and nonspecificity. That is, materials other than the hazardous materials may present a hydrogen peroxide demand.

In some cases, reaction intermediates may be toxic or less amenable to further treatment. These intermediates may arise from the oxidation of compounds in the waste stream that are not among the volatiles which the pretreatment is designed to eliminate. In addition, the relatively expensive oxidant may be used to partially or completely oxidize other compounds present in the waste stream in preference to those for which the pretreatment is designed. This will have the effect of increasing chemical requirements.

The removed component is ordinarily converted to another soluble material and remains in solution. Reduced sulfur compounds are generally oxidized to sulfate. Cyanide is oxidized to the less toxic cyanate. Organics are progressively oxidized, phenol for example is reported to be converted to catechol or hydroquinone, which are then further oxidized, reaction conditions permitting to carboxyllic acids and ultimately to carbon dioxide.


12 g/L H_2O_2
100 mg/L Fe^{++}
Wastewater
4 g/L phenol
25 g/L COD
Treated Effluent
phenol <8 mg/L
COD 12.5 g/L

Source: Sims 1981

Figure 5-2. Treatment of paint stripping effluent with hydrogen peroxide.

Laboratory determinations of the effectiveness of hydrogen peroxide treatment are required for individual waste streams, even if the chemical of interest is treatable in other streams. In addition, the need for catalysts, pH adjustment, and optimal residence time must be determined in the laboratory.

5.2.2.1.2 Ozone--Ozone treatment is carried out chemically in the same manner as hydrogen peroxide treatment, i.e., the oxidant reacts with organics or inorganic components in a waste stream to either partially or totally oxidize them. Depending on the characteristics of the waste stream and the degree of pretreatment required, the oxidant may be added to the waste in a holding tank and allowed to react, added to a pipeline upstream of the waste receiving tank, or if emissions from a storage tank are to be controlled, it can be added to the storage tank as necessary.

For this process, ozone is generated on site by the user. Ozone generation equipment is made by a number of manufacturers (e.g., Crane, Eimco, Emery, and Weisbach). The basic process for generating ozone passes air or oxygen through a high voltage arc. Typical operating efficiency is about 150 g ozone generated per kw-hr (Weber 1972). The ozone is ordinarily bubbled into the waste stream with a diffuser.

The principal industrial waste application for ozone treatment is the oxidation of cyanide. Pilot plant studies of ozonation of blast furnace wastewater which contains appreciable amounts of cyanide have been conducted by Osantowski et al. (1980). Roth and Murphy (1979) reported on laboratory studies of ozone treatment of TNT manufacturing wastewater, in the presence of ultraviolet light. Butkovic et al. (1983) have reported the rapid destruction of polynuclear aromatic hydrocarbons upon contact with ozone in water. In laboratory experiments they found half-lives of less than one second for benzo (a) pyrene and pyrene in the presence of 10^{-4} M ozone. Recent laboratory studies have addressed phenol (Otake et al. 1979), nitrilotriacetate (Ganes et al. 1980), and cyanide (Zeevalkink et al. 1980) destruction using ozone.

Ozone is generally introduced into the waste stream in conjuction with the air or oxygen stream from which it is generated. The ozone concentration from the generator is less than 1 percent. Thus, a substantial volume of air is bubbled through the wastewater. If emissions of VOCs from the wastewater are significant enough to require pretreatment, then the exhaust air stream may require some level of air pollution control. The advantages of ozone treatment include rapid reaction rate which results in small reactors and low space requirements. In addition, no sludges or concentrated waste streams are produced. The disadvantages include high operating costs, possible oxidation of materials other than the intended ones in complex streams. For very complex waste streams it is likely that ozone demand presented by compounds other than the specific compounds responsible for the volatile emissions may limit the application of this technology. It is also possible that ozonation may produce partially oxidized reaction intermediates that may be more toxic or more refractory to downstream treatment (although possibly less volatile).

In the past, ozone has been applied in the treatment of industrial cyanide and phenol wastes. There is evidence that organics including polynuclear aromatic commpounds can be treated by this method.

For specific waste streams, the uncertainties of ozone pretreatment include ozone requirements, the extent of reaction, and possible health and environmental effects of reaction intermediates.

5.2.2.1.3 Potassium Permanganate--Potassium permanganate can be added to wastewater in solid form and allowed to dissolve, or it can be mixed in aqueous solution and metered into the waste stream as needed. Necessary equipment is similar to that required for hydrogen peroxide oxidation (i.e., pumps and holding tanks). As potassium permaganate is used it forms an insoluble residue, manganese dioxide, that must be removed by filtration, prior to discharge or reuse. This additional process step adds to the complexity and cost of the process.

Potassium permanganate is rarely used for industrial waste treatment although it is frequently used in potable water treatment for removal of taste and odor. In laboratory studies, it has been found to oxidize phenol and hydrogen sulfide (Weber 1972) and the pesticides diquat and paraquat (Gomaa et al. 1971). Lenouette (1977) reported that potassium permanganate treatment was feasible for low concentrations of phenol and he recommended an oxidant to phenol ratio of 6 to 1.

Processing schemes for potassium permanganate treatment of wastewater are similar to those of hydrogen peroxide with the exception of an additional filtration step for removal of insoluble manganese dioxide.

The disadvantages of this process are the high chemical cost associated with its use on concentrated streams, incomplete oxidation of the specific compound of interest in a complex waste stream, possible production of more toxic (though less volatile) reaction intermediates, and the requirements for separation and disposal of sludges. Advantages are low capital costs and a high degree of flexibility in cases of fluctuating flows and concentrations.

The potassium permanganate process is most suitable for treatment of dilute waste streams with relatively low permanganate demand. One case where potassium permanganate treatment is particularly applicable is in the joint removal of phenol and soluble lead. Lead ions can be converted to insoluble lead oxide and this material can be removed in the filtration step.

5.2.2.1.4 Chlorine and Derivatives--Chlorine and sodium or calcium hypochlorite are widely used in the treatment of potable water and sanitary wastewater. For industrial waste treatment, the primary application has been the oxidation of cyanide. Chlorine gas is dissolved into the wastewater and reacts in solution. Sodium and calcium hypochlorite are generally bought in solution form and metered into the wastewater. These chemicals can be added to the wastewater in a reaction vessel or in a pipe leading to a storage vessel (if sufficient reaction time is permitted). If emission reduction from a storage vessel is the goal of pretreatment, chlorine can be added directly to the storage vessel. Oxidation of cyanide is carried out in alkaline solutions, and sodium hydroxide is generally used for initial pH adjustment. When chlorine gas is used, additional sodium hydroxide is required to maintain alkaline conditions.

The advantage of chlorine or hypochlorite treatment is that the reaction is fast (for cyanide) and thus requires low residence times (small reactor volumes and low land requirements). A major disadvantage of this treatment is the probable conversion of organics in the waste stream to hazardous chlorinated compounds. In some cases, these compounds have, high toxicity and present taste and odor problems even at very low concentrations. They may also be resistant to biological oxidation. In addition, chlorine storage and handling present certain safety problems which, although easily managed in a chemical plant, are not presented by the other oxidants.

Chlorine pretreatment is most suitable for cyanide- and ammonia-containing wastewater generated in the manufacturing and processing of metals. If the pretreated wastewater is subsequently used for cooling water, the chlorine residual may have a beneficial effect in preventing the growth of microorganisms on heat transfer surfaces. If the pretreated wastewater is to be ultimately discharged, the chlorine residual may require removal--a process typically done with activated carbon.

The oxidation of volatiles using chlorine does not produce concentrated waste streams or sludges. If metal ions are present in the wastewater, these may form insoluble salts under alkaline chlorination. In this case, a metal sludge will be formed which must be removed by filtration or settling. If these metals are to be ultimately removed, this may be an advantage.

5.2.2.2 Existing Sites--

A list of industrial applications of chemical oxidation is given in Table 5-3.

5.2.2.3 General Economics--

Osantowski et al. (1980; 1981) conducted pilot-scale studies of alkaline chlorination of blast furnace wastewaters and coke plant wastewaters for removal of cyanide and ammonia. Based on a 30-minute contact time, they estimated treatment costs of between $17 and $20 (1981 $) per 1,000 gallons of coke plant wastewater. Chemical costs were typically over 80 percent of the total annualized costs. Based on a 20-minute contact time they estimated treatment cost of $2.00 to $3.00 (1980 $) per 1,000 gallons of blast furnace wastewater. Chlorine gas was found to be more economical than sodium hypochlorite for this application.

5.2.3 Example Case

5.2.3.1 WET Streams Chosen--

Stream 01.02.04 "Spent Electroless nickel plating process solution" has been chosen as an example of ozone treatment. This stream contains 6 mg/L of cyanide and is produced at the rate of 30 kg/day.

TABLE 5-3. APPLICATIONS OF CHEMICAL OXIDATION

- Hydrogen Peroxide
  - Sanitary sewers
  - Municipal wastewater pumping stations
  - Municipal wastewater treatment plants
  - Refineries
  - Tanneries
  - Pharmaceutical manufacturing
  - Tin plating
  - Paint stripping
- Ozone
  - Coke plant wastewater
  - Iron and steel wastewater
- Chlorine and Derivitives
  - Blast furnace wastewater
  - Coke plant wastewater
  - Electroplating wastewater

Stream 01.02.02 "Spent cleaning and electroplating process solution" has been chosen as an example of chlorination. This stream contains 75 mg/L of cyanide and is produced at a rate of 1200 kg/day.

5.2.3.2 Process Details--

Process flow sheets for the two examples are given in Figures 5-3 and 5-4. Mass balances for these examples are given in Tables 5-4 and 5-5.

The main uncertainties in these examples are the degree of excess reactant that must be added, and the required residence time. These are influenced by the composition of the waste stream, i.e., by the presence of materials other than the cyanide which is the hazardous component to be treated.

The design variables include dosage of oxidant and reactor configuration as well as choice of oxidants.

5.2.3.3 Economics--

The volumemetric flow rate of stream 01.02.02 is very low. For comparison purposes the costs of treatment of a stream of 100 times this volume have been estimated, based on the data of Osantowski (1981). Treatment of a waste volume of 120,000 kg/day would require a capital investment of $270,000 (1980) with annual operating costs of $220,000. This would achieve 99 percent removal of cyanide from the wastestream.

5.2.4 Advantages and Disadvantages

The advantages of chemical oxidation are its relatively low capital cost and high flexibility. Chemical addition rates can be adjusted to handle surges and process upsets. During low-flow or low-concentration operating periods, chemical additions can be cut back. Systems can be installed quickly, in some cases by moving a drum of oxidant and a metering pump to an existing process vessel.

The disadvantages of chemical oxidation are the relatively high operating cost (chiefly composed of chemical costs) and the potential waste of chemicals in oxidizing of components other than the hazardous component of interest. In many cases, an oxidant demand must be satisfied in the wastewater before oxidant will be available to react with the hazardous material. The possibility of forming toxic or hazardous intermediates (particularly

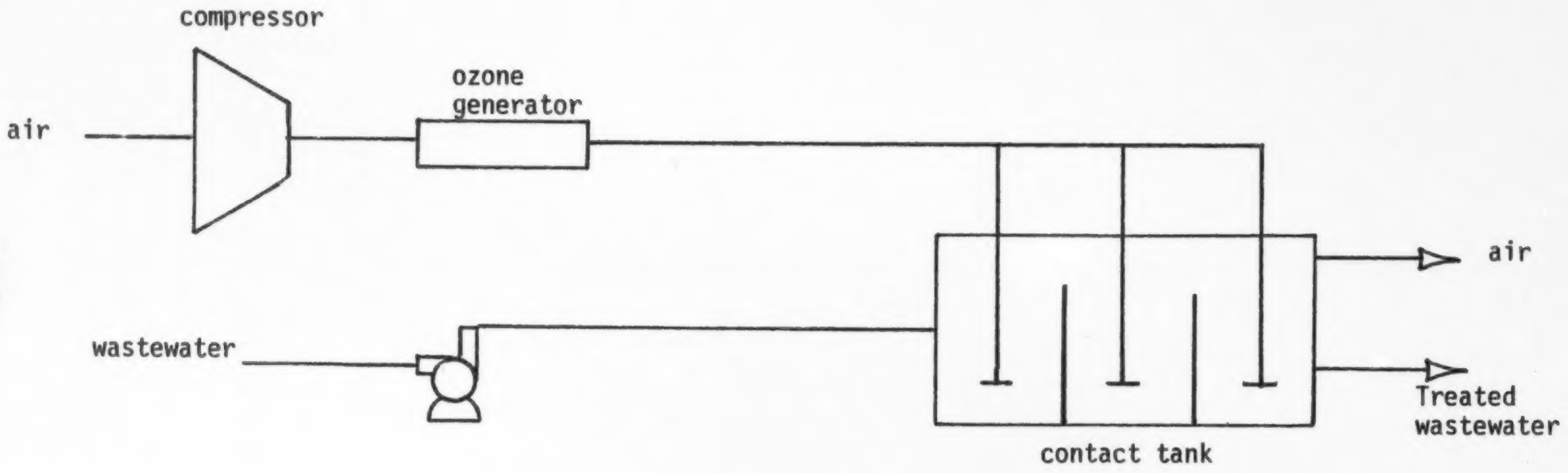
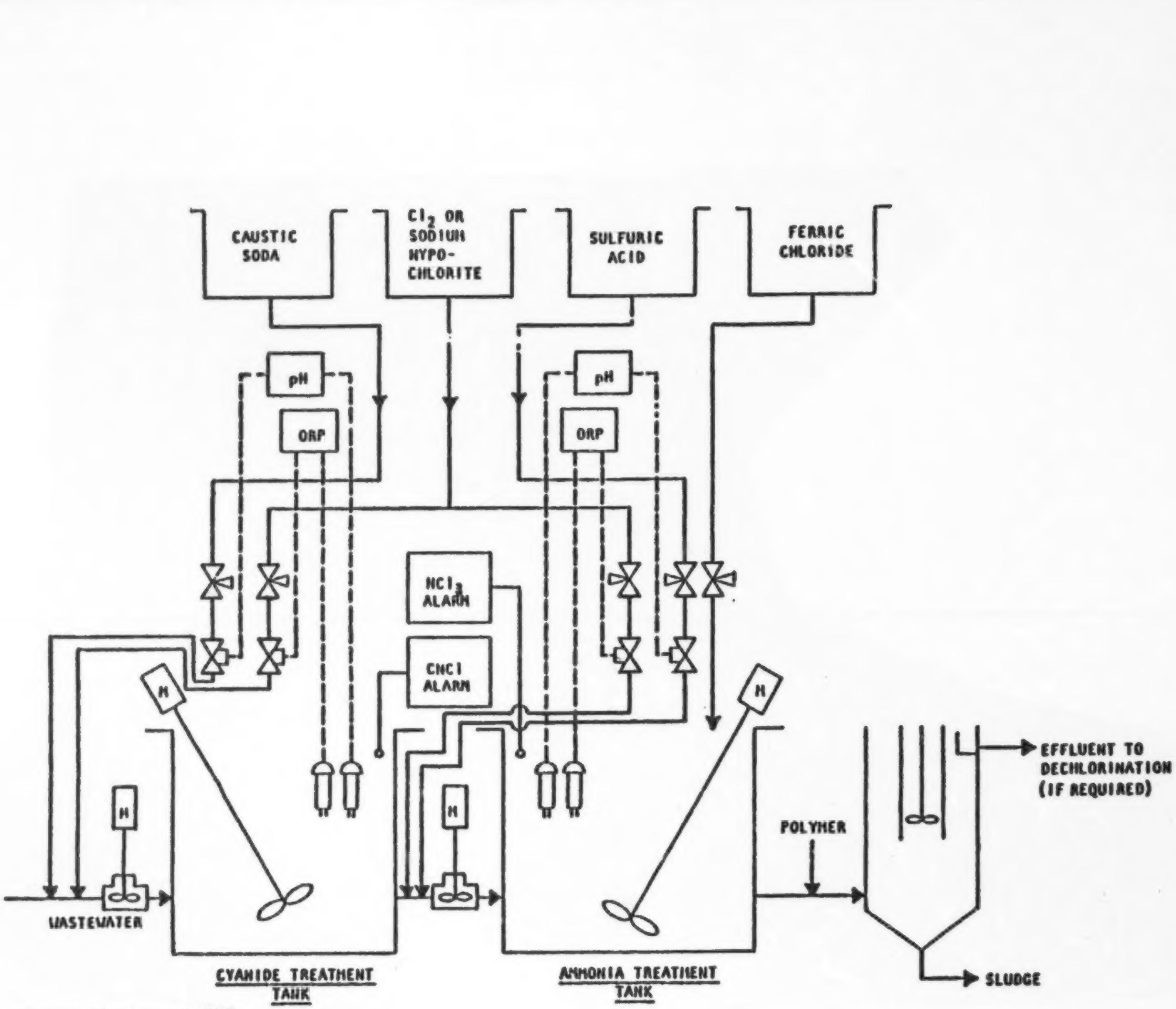

compressor
air
ozone
generator
wastewater
air
Treated
wastewater
contact tank

Figure 5-3. Process flow sheet for ozone pretreatment of WET stream 01.02.04.

TABLE 5-4. MASS BALANCE FOR OZONE TREATMENT OF STREAM 01.02.04

	kg/Day
IN:	
Wastewater	27.2
Cyanide	0.002
Air	6.0
OUT:	
Treated wastewater	27.2
Cyanide	0.00002
Air	6.0


CAUSTIC SODA
Cl_2 OR SODIUM HYPO-CHLORITE
SULFURIC ACID
FERRIC CHLORIDE
pH
ORP
pH
ORP
NCl_3 ALARM
CNCl ALARM
M
M
M
M
EFFLUENT TO DECHLORINATION (IF REQUIRED)
POLYMER
WASTEWATER
CYANIDE TREATMENT TANK
AMMONIA TREATMENT TANK
SLUDGE

Source: Osantowski 1980

Figure 5-4. Process flow sheet for chlorine pretreatment of WET stream 01.02.02.

TABLE 5-5. MASS BALANCE FOR ALKALINE CHLORINATION OF STREAM 01.02.02
(Spent Cleaning and Electroplating Process Solutions)

	kg/Day
IN:	
Wastewater	1200
Cyanide	0.09
Chlorine	0.26
Sodium hydroxide	0.28
OUT:	
Wastewater	1200
Sodium cyanate	0.15
Chlorine	0.012
Sodium chloride	0.41

when chlorine and its derivatives are used) is a serious concern. The effect of partial oxidation of the hazardous material upon further processing must also be evaluated.

5.2.5 Recommendations for Further Study

Individual laboratory testing of waste streams must be conducted to optimize oxidant addition rate, temperature, pH, residence time, etc. In addition, the treated effluent must be analyzed to determine the presence or absence of reaction intermediates.

5.3 ADSORPTION

5.3.1 Introduction

Adsorption is one of several techniques that may be used as a pretreatment method to control volatile emissions from hazardous waste streams. The choice of adsorption as a pretreatment technique and the design of the actual adsorption process system depend upon, among other factors, the physical/chemical characteristics, quantity treated, and variability of the hazardous waste stream. This section examines various adsorption process systems that may be used for hazardous waste pretreatment and the types of hazardous waste streams for which these systems would be technically feasible.

The adsorption of organic compounds from both liquid and gaseous phases onto activated carbon is a mature process technology with widespread use as an integral unit operation in such industrial manufacturing processes as corn syrup and pharmaceuticals production, and sugar refining; industrial and municipal wastewater treatment; drinking water purification; the separation and recovery of organic compounds from vapor streams; and pollution control of atmospheric emissions. Although activated carbon has been and continues to be the dominant adsorbent used, other adsorbents such as resin or polymeric materials and zeolite molecular sieves have found increasing use for a number of special applications in recent years.

Since the selection of a pretreatment process depends on the nature of the hazardous waste stream, a number of different process configurations incorporating adsorption methods may be devised to accommodate a broader spectrum of hazardous waste streams. For this discussion, adsorption processes may be broadly classified into two groups: liquid phase and gas phase adsorption processes. Within these two groups there are several major process types that can be used for hazardous waste pretreatment to control volatile emissions. In addition, each process type may have several design variations so that the process can be tailored to specific situations. For example, different types of contactors (adsorbers) and adsorbent regeneration schemes can be used in a liquid phase carbon adsorption system.

For liquid phase adsorption, activated carbon and resin systems are the two basic types of interest. A third type, ion exchange, which is a special type of resin adsorption system where only ionic species are removed from the liquid phase, will not be considered here. Aside from the obvious difference in the type of adsorbent used, the major distinction between carbon and resin adsorption systems is the type of adsorbent regeneration process employed. The resin adsorption systems rely exclusively on solvent extraction or washing to regenerate the adsorbent. For carbon adsorption systems, several regeneration methods are possible. Possible methods are: once through carbon (no regeneration), thermal regeneration, and solvent extraction or washing. In the carbon adsorption systems thermal regeneration predominates.

Gas phase adsorption systems (for pretreatment of hazardous wastes) include processes where volatile constituents are separated from the hazardous waste stream into a gaseous stream for subsequent removal by adsorption. These gas phase pretreatment systems serve as a volatile constituent removal system for materials removed from hazardous waste streams. This allows adsorption to be used on slurries and sludges that cannot be treated by liquid phase adsorption. The phase separation processes coupled with an adsorption process that will be considered here include air/steam stripping and evaporation. For these gas phase systems, activated carbon is the predominant adsorbent, and it will, therefore, serve as the basis of the discussion here. Other adsorbents such as resins find limited use in gas phase adsorption because they are less cost effective than activated carbon.

5.3.2 Liquid Phase Carbon Adsorption

5.3.2.1 State of the Art--

Carbon adsorption is a mature technology whose beginning can be traced back more than 3,500 years to the use of bone chars for their medicinal properties. Modern adsorption technology, however, began in the late 19th century when the decolorizing and gas separation properties of chars were first investigated. These investigations led to the introduction of commercial activated carbons in the early part of the 20th Century. The early development of these carbons was promoted by decolorizing applications in the sugar industry and by the need to develop adsorbents that would provide protection against poison gases used in World War I.

The intensive effort to develop carbon filters for gas masks provided the impetus to search for other applications of carbon adsorption. The first important industrial use of activated carbons occurred in sugar refining to decolorize the sugar syrup. Initially, powdered activated carbons (PAC) on a once-through-throw-away basis were used. Over the last 20 years, however, the increased cost of activated carbons and the disposal of spent PAC, which is difficult to regenerate, has prompted a shift toward regenerable granular activated carbons (GAC) in sugar refining and other industrial processes that involve decoloring operations such as uranium recovery processing in phosphate mining.

Since the first introduction of carbon adsorption in a municipal wastewater treatment facility (at South Lake Tahoe, California in 1965), this treatment method has been widely adopted in both industrial and municipal wastewater facilities throughout the United States. The South Lake Tahoe facility operated continuously over 15 years with onsite regeneration of the GAC in a multihearth furnace. Its performance has verified the results of bench-scale reactivation tests (made in 1963), indicating that the GAC could be maintained at or near full adsorptive capacity by means of thermal reactivation until the carbon was eventually replaced due to losses from attrition and burnoff. The plant also demonstrated that the GAC has a service life of at least 12 reactivation cycles under full-scale plant operating conditions.

For over 50 years, PAC has been used to control the taste and odor in drinking water purification facilities. The PAC is added to the raw water ahead of filter beds; quality control tests determine the quantity of PAC required to eliminate any taste and odor. Typical PAC dosages ranged 5 to 10 mg/L for most drinking water supplies with up to 50 mg/L for water sources having high levels of taste and odor. The PAC which is removed from the water in the filter beds is disposed of as a solid nonhazardous waste.

In the 1970's concern over the presence of trihalomethanes (THM) in drinking water led to the introduction of GAC systems into water purification facilities. Trihalomethanes are typically found at ppm levels and are the result of water chlorination for disinfection. The chlorine reacts with humic acid substances normally present in surface water supplies to form the trihalomethanes. To demonstrate the technical feasibility and to develop capital and operating cost data, EPA provided funding for the construction and operation (for a limited period) of GAC demonstration plants with onsite carbon regeneration. These demonstration water treatment plants at Manchester, New Hampshire, and Cincinnati, Ohio, were designed to reduce trihalomethanes to ppb levels.

In addition to the municipal wastewater and drinking water facilities that use carbon adsorption treatment, many industrial plants employ carbon adsorption methods to control of organic emissions, recover organic solvents, and treat wastewater. Information about commercial applications of GAC systems is presented in Section 5.3.2.1.3.

5.3.2.1.1 Process description--

Principle of Operation--Activated carbon (AC) is the generic name given to the class of amorphous carbons that have been specially treated to yield a microporous structure within the solid particle. These internal micropores, which typically range from 10 to 100 Angstroms in radius, provide the large surface areas of 500 to 1,500 m^2/g that give activated carbons their high adsorptive capacities. The distribution of this internal surface area by pore size is a major factor affecting the carbon's adsorptive characteristics. For example, if the distribution of pore sizes is skewed toward the larger pore sizes, i.e., a significant fraction of the surface area is associated with the larger pores, the carbon has an enhanced capacity for large adsorbate molecules. This type of AC is generally referred to as a "decolorizing" carbon. When the pore size distribution is skewed toward the smaller pores, the carbon has an enhanced adsorptive capacity for small molecules, and the carbon is called a "gas phase" carbon.

Although most of the carbon's surface is nonpolar in nature, the interaction of the surface with oxygen during production and storage does yield active sites or chemical groups that do give the surface a slightly polar nature. The degree of surface polarity is important to the carbon's adsorptive properties, particularly in liquid phase adsorption. The generally low surface polarity of carbon accounts for its preferential adsorption of nonpolar species.

In principle, activated carbons can be made from any solid or highly viscous carboneous raw material including both natural and man-made materials. Commercial activated carbons, however, are generally made from coal, wood, coconut shells, pulp mill residues, petroleum base residues, and char from sewage sludge pyrolysis. The microporous amorphous carbon structure is developed through carefully controlled treatment processes of dehydration, devolatilization (carbonization), and oxidation (activation or burnoff).

The adsorption of molecules on activated carbon is the result of interactions between the molecular forces of the adsorbate and the unbalanced surface forces of the carbon. In the adsorption of organic materials (e.g., volatile constituents of waste streams), the predominant interacting forces are dispersion forces. Since no chemical bonds are formed in dispersion force interactions, this type of adsorption between the adsorbate and the carbon surface is termed "physical" adsorption and has associated with it an exothermic heat to adsorption that is of the order of magnitude of the adsorbate's heat of vaporization. This physical adsorption is reversible and allows the regeneration or reactivation of the carbon surface.

Although physical adsorption is the dominant mechanism for the adsorption of organics on activated carbon, a small fraction of adsorbate molecules generally form chemical bonds with reactive groups or sites on the carbon's surface. This type of adsorption, which is called "chemisorption," is not reversible since the adsorbate cannot be removed from the surface that was adsorbed. Chemisorption occurs primarily on virgin activated carbon (new carbon that has never been in adsorption service) and freshly regenerated carbon that has been thermally regenerated at temperatures above 1400° F in a steam/oxygen atmosphere.

In liquid phase adsorption, if adequate carbon-solution contact time is provided, an equilibrium is established in which the rates of solute adsorption and desorption are equal. The amount of solute adsorbed per unit weight of carbon increases as the concentration of the solute in the solution increases. For a particular solution-carbon system, this equilibrium is set, in general, by two types of interactions: solute-adsorbent and solute-solvent. This means that the forces favoring dissolution and the forces favoring adsorption are competing; thus, any change in the solution-carbon system that decreases the solute-solvent interaction forces and increases the solute-carbon interaction forces will shift the equilibrium toward higher adsorption per unit weight of carbon.

In view of the above interactions that affect liquid phase adsorption on activated carbon, the following general rules should guide the selection and design of a hazardous waste pretreatment system:

- Higher carbon surface areas yield higher adsorption capacity.
- Larger micropore sizes yield higher adsorption capacity for large molecules.
- Adsorptivity increases as the solubility of the solute in the solvent decreases; therefore, for hydrocarbons, adsorption increases as molecular weight increases.
- For solutes with ionizable groups, maximum adsorption occurs at the pH corresponding to the minimum ionization.
- Since adsorption is a exothermic process, adsorption decreases with increasing temperature. In liquid phase adsorption, however, this effect is generally small.
- The carbon's adsorption capacity for a specific solute depends on the type and concentration of other adsorbable solutes in the solution. Higher molecular weight hydrocarbons tend to displace the lower molecular weight species on the carbon. This can result in effluent concentrations which are higher than influent concentrations for the lower molecular weight species.

The above discussion refers exclusively to adsorption capacity, a thermodynamic property, and it does not account for adsorption kinetics which is of equal importance in adsorption system design. In some cases thermodynamic and kinetic adsorption factors have competing effects on system performance, and appropriate tradeoffs must be made in process design. For example, while adsorption capacity increases as hydrocarbon molecular weight increases, the rate of adsorption decreases. Similarly, while an increase in temperature decreases adsorption capacity, it may--depending on the rate-controlling mechanism for the overall process--increase the rate of solute removal from solution.

Another factor that must be considered in liquid phase carbon adsorption is the biological activity that usually occurs in the carbon bed when (1) the concentration of adsorbed species is high enough and (2) the adsorbate is biodegradable and nontoxic to bacteria that may be present in the feed stream. If biological degradation does occur, a significant increase in the capacity of the carbon bed may result. Because time is required for the bacteria to become acclimated and grow to a significant concentration, biological activity does not usually become important until after many hours of operation. But, this effect can be substantial. In some reported cases, the adsorptive life is doubled.

Basic Process Configurations--The liquid phase activated carbon adsorption process involves two basic steps as shown in Figure 5-5. In Step 1 (adsorption), the waste stream contacts the carbon which selectively adsorbs the hazardous material(s) and allows the purified stream to pass through. Step 2 (disposition of contaminated or spent carbon) represents a number of process options. When the carbon reaches its maximum capacity or when the effluent is unacceptable for discharge, i.e., when breakthrough of the hazardous material(s) occurs, the carbon is removed from the adsorber for disposal, destruction, or regeneration as established by the option selected under Step 2. In some cases, the carbon can be regenerated in such a way that the adsorbate(s) is(are) recovered.

Under Step 2 there are three basic options available for handling the spent carbon from the adsorber:

1. Direct disposal of the contaminated carbon in a landfill. In this case pollution of water and air can occur.

2. Regeneration of the carbon with destruction of the hazardous waste. In this case, secondary emissions to the environment such as CO_2, ash, and heat must be handled. The regenerated carbon is recycled to the adsorber.

3. Regeneration of the carbon with reclamation of the hazardous waste. In this case, some secondary waste streams may have to be handled in reclaiming the hazardous waste. The regenerated carbon is recycled to the adsorber.

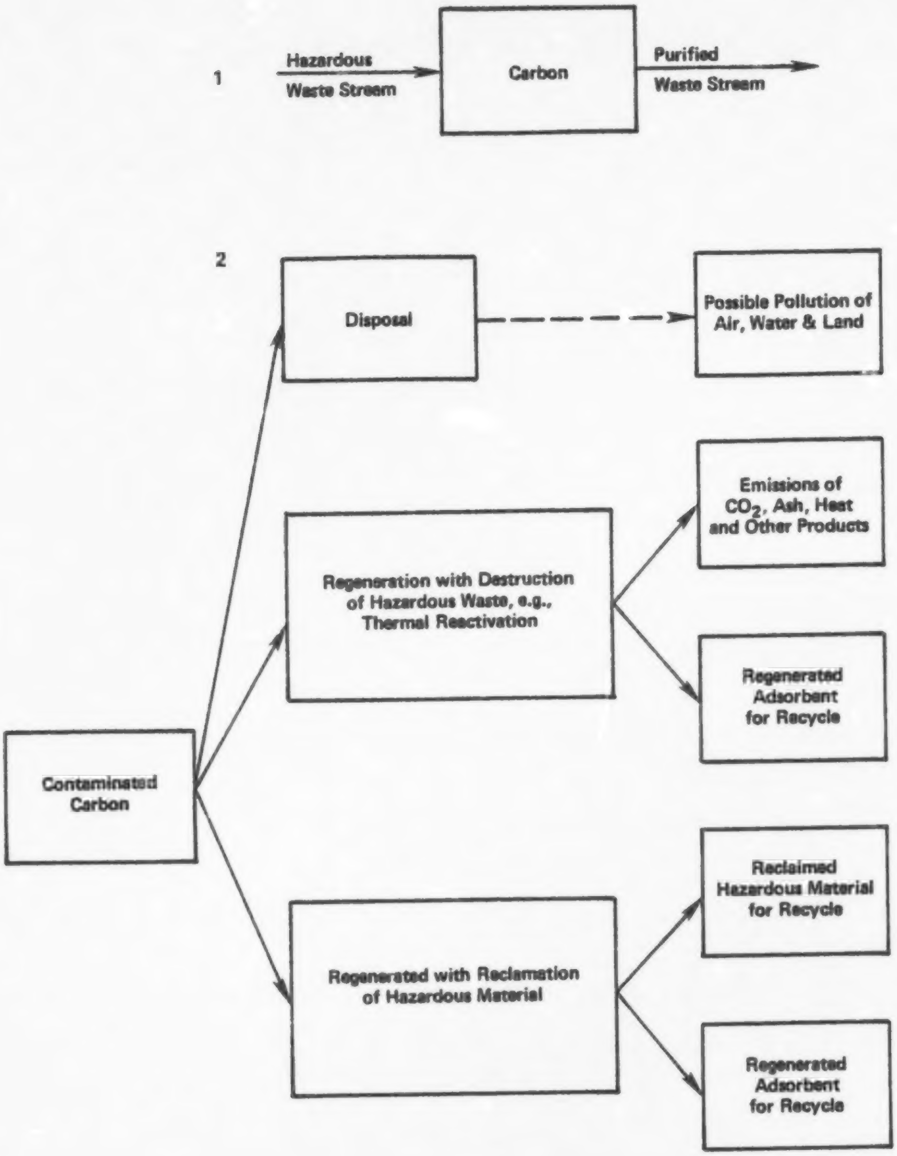

1
Hazardous
Waste Stream
Carbon
Purified
Waste Stream
2
Disposal
Possible Pollution of Air, Water & Land
Emissions of CO_2, Ash, Heat and Other Products
Regeneration with Destruction of Hazardous Waste, e.g., Thermal Reactivation
Regenerated Adsorbent for Recycle
Contaminated Carbon
Reclaimed Hazardous Material for Recycle
Regenerated with Reclamation of Hazardous Material
Regenerated Adsorbent for Recycle

Figure 5-5. Steps in carbon adsorption.

5-5

Contacting Processes--In the adsorber section of the carbon system, there are four basic liquid-carbon contacting processes: (1) adsorbers in parallel, (2) adsorbers in series, (3) moving bed, and (4) upflow-expanded bed. The choice of the contacting process depends on the physical characteristics of the waste influent, the effluent criteria, throughput requirements, and economics. Figure 5-6 illustrates these four contacting processes and Table 5-6 lists some of the distinguishing features of each process.

In the above contacting processes, flow rates are typically in the range of 2 to 10 gal/min/ft^2 for downflow operation, 2 to 7 gal/min/ft^2 for upflow operation without bed expansion, and around 15 gal/min/ft^2 for upflow-expanded with about 15 percent bed expansion. Downflow operation may be either by gravity or pressure; the former is clearly less expensive but only applicable if the concentration of suspended solids in the influent is low.

Except for the moving bed, the other three contacting processes are basically batch-type operations. At various times one or more of the adsorber units (adsorption vessels) is out of service while the carbon is either removed (for disposal or external regeneration) or being regenerated in situ. The moving bed process, which provides the most efficient utilization of the carbon, is a semi-continuous process.

In the moving bed or "pulsed" bed adsorber, the waste stream and the carbon are contacted countercurrently; the liquid flows upward through the bed, which is slightly expanded, and the carbon moves downward. The carbon movement is not continuous but occurs as discrete pulses. This downward movement is accomplished by momentarily interrupting the waste stream upward flow, opening a valve at the bottom of the column, and introducing a premeasured volume of slurried carbon at the top of the column. This pulse of fresh carbon displaces an equal volume of spent (contaminated or loaded) carbon at the bottom of the column. The spent carbon is then regenerated and recycled to the top of the adsorber column. After the pulse movement of the carbon bed, flow of the waste through the adsorber is restored. As a result of this countercurrent flow pattern, the liquid phase leaving the top of the adsorber, which has the lowest concentration of contaminants, is contacted with carbon having the least amount of adsorbed material last, thereby providing the mazimum driving force for adsorption. Although this

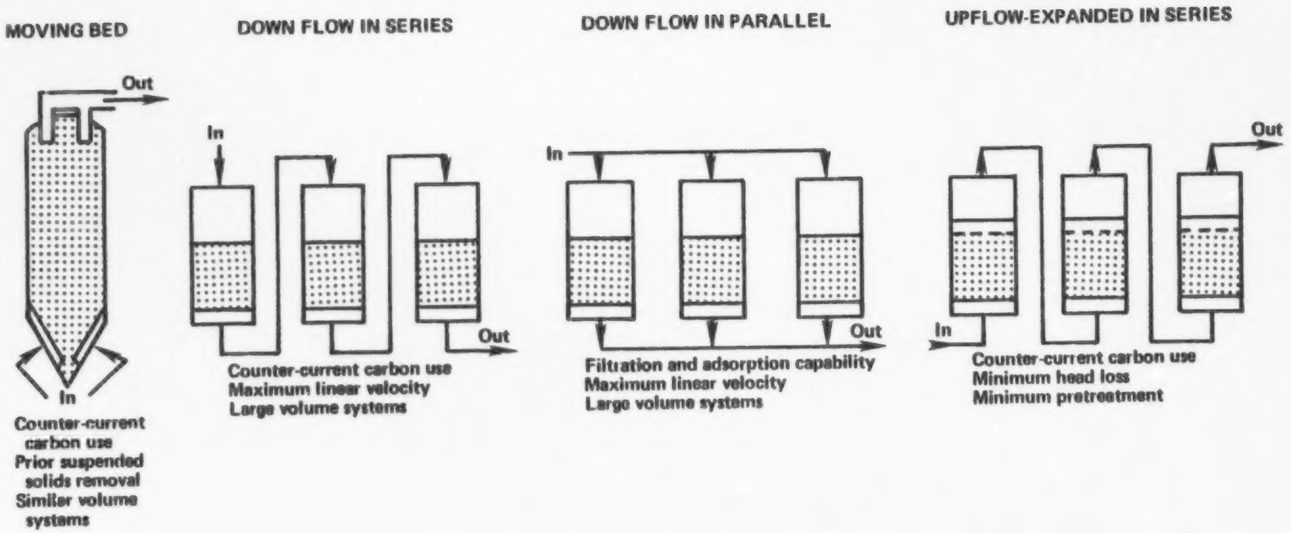

MOVING BED
DOWN FLOW IN SERIES
DOWN FLOW IN PARALLEL
UPFLOW-EXPANDED IN SERIES
Out
In
Counter-current carbon use
Prior suspended solids removal
Similar volume systems
In
Out
Counter-current carbon use
Maximum linear velocity
Large volume systems
In
Out
Filtration and adsorption capability
Maximum linear velocity
Large volume systems
In
Out
Counter-current carbon use
Minimum head loss
Minimum pretreatment

Figure 5-6. Carbon adsorber configurations.

TABLE 5-6. CHARACTERIZATION OF CARBON CONTACTING METHODS FOR HAZARDOUS WASTE TREATMENT

Method	Comments
ADSORBERS IN PARALLEL	• For high volume applications • Can handle higher than average suspended solids (~65-70 ppm) if downflow • Relatively low capital costs • Effluents from several columns blended, therefore less suitable where effluent limitations are low
ADSORBERS IN SERIES	• Large volume systems • Countercurrent carbon use • Effluent concentrations relatively low • Can handle higher than average suspended solids (~65-70 ppm) if downflow • Capital costs higher than for parallel systems
MOVING BED	• Countercurrent carbon use (most efficient use of carbon) • Suspended solids must be low (< 10 ppm) • Best for smaller volume systems • Capital and operating costs relatively high • Can use such beds in parallel or series

(continued)

TABLE 5-6 (continued)

Method	Comments
UPFLOW-EXPANDED	• Countercurrent carbon use (if in series) • Can handle high suspended solids (they are allowed to pass through) • High flows in bed (~ 15 gal/min/ft^2)

moving bed adsorber design is the most efficient of the four contacting processes, it is also the most complex and expensive process.

In the other downflow adsorbers, waste stream flow must be periodically interrupted and the carbon column backwashed with water. This backwashing removes suspended solids that have been filtered out of the liquid by the carbon bed. Downflow contactors have been designed to act in part as filters for suspended solids and they require frequent backwashing with bed expansions up to 50 percent. To minimize the frequency of backwashing, the suspended solids level of the influent should be less than 50 ppm. At this concentration the typical downflow contactor will require one backwashing per day. Higher suspended solids levels of 2,000 ppm and above can be handled in downflow contactors, but at a cost of more frequent backwashing. Frequent backwashing reduces overall column throughput rate and increases the amount of backwash water that must be treated. This backwash water is usually treated by sedimentation.

Carbon Regeneration Processes--When the carbon's capacity is exhausted in the adsorber, the carbon must either be replaced with new carbon or regenerated (reactivated) and reused. If the carbon usage rate for the particular facility is large, typically above 1,000 lb/day, then carbon regeneration is usually economically feasible. This regeneration of the carbon is accomplished either by thermal treatment in which the organic adsorbate is destroyed or by non-destructive chemical treatment. Thermal regeneration is the most widely used of these methods. Some of the carbon regeneration options are briefly described below.

1. Thermal Regeneration: In this method the spent carbon is removed from the adsorber and regenerated with steam in high temperature processing equipment such as a multihearth furnace, a rotary kiln, or a fluidized bed furnace at temperatures from 870° C to 980° C. Typically thermal regneration requires about 1-2 lb steam/lb carbon, about 4,000-5,000 Btu of fuel/lb carbon, and a furnace residence time on the order of 30 minutes. With proper control of the regeneration conditions carbon losses from the burning away of the carbon itself can be generally held within 4 to 9 percent. This carbon loss is made up with virgin carbon. The organic adsorbate is vaporized and partially burned in the regenerating furnace. To insure

complete destruction of the devolatilized adsorbate, the furnace effluent gas is passed through afterburners followed by a scrubber to remove particulate and noxious combustion products, such as HCl from halogenated organics. An additional 2,000-4,000 Btu/lb of carbon is required to operate the afterburners.

In some circumstances thermal regeneration of GAC is not possible, e.g.,

- When inorganic salts have deposited (or may deposit) on the carbon, although an acid prewashing step before thermal regneration may mitigate this situation;
- When the carbon contains adsorbates that would cause air pollution problems upon regeneration (e.g., NO_x, radioactive wastes, etc.);
- When the adsorbates are explosive (e.g., TNT);
- When the loaded carbon is excessively corrosive.

2. Alkaline Regeneration for Acid Adsorbates: In some waste streams where the major organic component is acidic, carbon adsorption may be carried out under acidic conditions and the carbon regenerated under basic conditions. Dow Chemical Company in Midland, Michigan has used this approach to recover phenol and acetic acid (Himmelstein et al. 1974; Fox et al. 1973). Sherwin Williams operates a large plant in which p-cresol is adsorbed from a stream and recovered by regenerating the carbon with a 10 percent NaOH stream (Minor 1974).

3. Acid Regeneration for Basic Adsorbates: Similar to basic regeneration, certain basic adsorbates that are adsorbed under basic conditions may be recovered by washing the carbon with acid. This method has been reported as a practical means of recovering ethylene diamine at Dow Chemical Company (Berkowitz et al. 1978).

4. Solvent Regeneration: In those cases where the adsorbate easily dissolves in an organic solvent, the adsorbate may be washed off the carbon and recovered after separation from the solvent, e.g., via distillation. Pilot-scale studies have shown that organics adsorbed from coke plant flushing liquor can be stripped from the carbon by a hot benzene wash (Loven 1974). A demonstration unit (150-175 gal/min) in which acetic acid is removed from carbon via a hot ethanol wash and recovered as ethyl acetate

was installed at the Flambeau Paper Company, Park Falls, Wisconsin (Berkowitz et al. 1978).

5. Steam Regeneration: If the adsorbate is highly volatile, carbon regeneration and adsorbate recovery may be accomplished by passing steam through the carbon bed and condensing the effluent. This method is commonly employed where carbon is used for gas-phase adsorption.

5.3.2.1.2 Process operation--

Applicable Feed Streams--The technical suitability of a waste stream for carbon adsorption pretreatment depends mainly on its physical form, and the type and relative concentration of constituents. However, other factors that impact treatment economics often dictate which streams are actually feasible for carbon treatment; such factors include the required degree of solute removal, waste throughput rate, and carbon utilization. The discussion below is intended to provide guidance in prescreening waste streams for carbon treatment. The actual selection should be based on laboratory adsorption and regeneration studies with the actual waste stream.

In general, carbon adsorption is applicable only to single-phase fluid streams, specifically, liquid solutions and gas mixtures. Although both aqueous and nonaqueous streams may be treated with carbon, waste treatment applications to date have been confined to aqueous streams. The nonaqueous streams that have been treated with carbon, primarily for color removal, include petroleum fractions, syrups, animal and vegetable oils, and pharmaceutical preparations.

The suspended solids level in the waste influent to the carbon contactors (adsorbers) generally should be less than 50 ppm for optimum process operation. At that level, one bed backwash a day is often sufficient to remove the accumulated solids and maintain bed pressure drop within its design range. Although suspended solid levels up to 2,000 ppm may be handled in downflow contactors, more frequent bed backwashing will be required. Waste streams containing suspended solid levels above 2,000 ppm may still be treated with carbon, if stream prefiltering is employed.

The amount and type of nonvolatile organics and dissolved inorganics must also be considered. Oil and grease in the waste stream should be less than 10 ppm to avoid carbon fouling. High levels of dissolved inorganics may cause such problems as scaling (corrosion) and serious loss of carbon activity with thermal carbon reactivation. In some cases, however, these problems may be mitigated through pH control and softening of the waste influent or by acid washing the carbon before reactivation.

Technically, a high concentration of solute(s) in the waste influent does not limit carbon adsorption treatment; however, in actual practice the most concentrated influent to be treated on a continuous basis contained approximately 10,000 ppm TOC. Nevertheless, historical practices do not preclude that higher solute concentrations can be carbon treated. Because the slopes of adsorption isotherms are nearly always positive, the carbon loading (weight fraction of solute on the carbon) increases as the influent solute concentration increases, thereby resulting in more efficient solute removal and carbon utilization. In addition, when the carbon is regenerated, the higher concentration influents may require less frequent regeneration. This latter benefit is particularly enhanced where the slope of the adsorption isotherm is greater than 1.

The quantity (flow rate) of the waste stream does not affect the technical aspects of carbon treatment, but it does have a major impact on treatment economics. Carbon treatment benefits significantly from economies of scale, especially where thermal reactivation is used. If carbon usage is less than 500 kg/day, then the economics generally favor disposal of the spent carbon. At carbon usage over 4,000 kg/day, onsite thermal reactivation is usually feasible. Where carbon rates are between 500 and 4,000 kg/day, offsite reactivation should be considered.

The identification of waste streams that are suitable for carbon treatment is more difficult when multicomponent solutes are present. Some "secondary" constituent may interfere with the adsorption of the solute(s) of interest. For example, long-chain organic soaps were found to cause poor carbon adsorption performance on a wastewater stream from a polyvinyl chloride production plant (U.S. EPA 1971). Thus, preliminary laboratory studies on the actual waste stream are essential in prescreening candidate waste streams for carbon treatment.

In summary, the following characteristics may be used as guidelines to identify wastes streams that are likely candidates for carbon treament:

- Aqueous waste streams with organic solute concentrations that are less than 1%
- Waste streams where the aggregate concentration of high molecular weight nonvolatile organics is substantially lower than the concentration of the volatile organics
- Waste streams where suspended solids are less than 50 ppm if the stream is not prefiltered, and less than 2.5% if prefiltering is used
- Waste streams where oil and grease concentrations are less than 10 ppm
- Waste streams where the concentration of dissolved inorganics is low (less than 100 ppm) unless waste stream preconditioning and spent carbon washing before reactivation operations are included.

Process Emissions and Wastes--In carbon treatment facilities where thermal carbon regeneration is used, no serious environmental impacts are encountered. The basic output streams include: (1) the treated waste effluent from the carbon contactors; (2) reactivation furnace offgas, which typically has been through afterburner and scrubber, and, in some cases, a dust filter; (3) scrubber effluent containing fly ash and possibly some halogenated or sulfur compounds (e.g. HCl and H_2SO_x); (4) suspended solids from prefilters and carbon contactor backwashing; and, in a few cases (5) exhausted carbon that cannot be regenerated to its prescribed operating capacity.

When chemical reactivation is used, the major output streams are: (1) the treated waste effluent; (2) the recovered waste solute(s); (3) the nonrecyclable portion of the reactivating solution or solvent; and (4) exhausted carbon that has gradually lost its adsorption capacity. Typically in chemical reactivation operations, the entire carbon inventory must be replaced periodically with fresh carbon. This exhausted carbon may be either landfilled or burned.

Removal Efficiency--The removal efficiency of carbon treatment can be controlled to any level through the design of the carbon contactor. Typical carbon treatment efficiencies are better than 99 percent with influent concentrations below 1,000 ppm. At higher influent concentrations, removal efficiencies can exceed 99.99 percent removal to yield effluent concentrations at several ppm. Of course as with most alternative treatment processes, carbon treatment removal efficiencies must be traded off against capital and operating costs which increase dramatically as efficiencies approach 100 percent.

State of Recovered Volatiles--When thermal carbon reactivation is used in the carbon treatment system, the volatiles are destroyed in the reactivating furnace and afterburner. In the chemical reactivation systems the volatiles are generally recovered in concentrated solution containing some of the reactivating constituent.

5.3.2.1.3 Existing sites--Table 5-7 gives a summary of industrial sources using GAC systems. Full-scale activated carbon systems treating organic chemical wastes are listed in Table 5-8, and industrial installations using GAC systems for wastewater treatment are listed in Table 5-9. The tabulation of facilities in these tables only represents a partial listing of systems that use activated carbon in liquid phase adsorption.

5.3.2.1.4 Process economics--Several variables and/or alternatives in the design and operation of a carbon treatment system can have a major impact on the economics of the process. These factors include:

- Type of carbon (GAC or PAC)
- Flow rate
- Contact time
- Process configuration (series, parallel, or moving bed)
- Number of stages
- Flow direction (packed or expanded; upflow or downflow)
- Hydraulic force (pumped or gravity)
- Method of reactivation (thermal, chemical, or none)
- Carbon capacity.

TABLE 5-7. SUMMARY OF INDUSTRIAL SOURCES USING GRANULAR ACTIVATED CARBON SYSTEMS

	Industry	Location	Principal Product	Contaminant(s) Removed
1.	Velvet Textiles	Blackstone, VA	Velvet	Dyes, detergents, organics
2.	BASF Wyandotte Chemical Corp.	Washington, NJ	Polyethers	Polyethers (MW 1,000 to 3,000)
3.	ARCO-Watson Refinery	Wilmington, CA	Refinery products	COD
4.	Stephen Leedon	Southhampton, PA	Carpet mill	Dyes
5.	Reichhold Chemicals, Inc.	Tuscaloosa, AL	Phenol, formaldehyde, pentaerythritol, orthophenylphenol, synthetic resins and plastics	COD, phenols
6.	Schenectady Chemicals, Inc.	Rotterdam, NY	Phenolic resins	Phenols
7.	Chipman Division of Rhodia, Inc.	Portland, OR	Herbicides-2,4-D acid, MCPA acid, 2,4-DB acid and esters of these products	COD, phenols
8.	Sherwin-Williams Co.	Chicago, IL	p-Cresol	p-Cresol
9.	Mobay Chemical Co.	Houston, TX	-	Color
10.	Burlington Army Ammunition Plant	Burlington, IA	Explosives	TNT
11.	Stepan Chemical Co.	Bordentown, NJ	Intermediate detergents	Color and organics
12.	Georgia Pacific	Conway, NC	Phenolic resins	Phenols
13.	Stauffer Chemical	Skanaeteles Falls, NY	Strong alkaline detergents	COD
14.	General Electric Co.	Selkirk, NY	Plastics	Phenols and COD
15.	C.H. Masland & Sons	Wakefield, RI	Carpet yarn	Color and COD
16.	St. Regis Paper	Pensacola, FL	Kraft products	Color
17.	Monsanto Industrial Chemicals	Anniston, AL	Intermediate organic chemicals (polynitrophenol)	Polynitrophenol
18.	Hercules, Inc.	Hattiesburg, MS	Acid resins, turpentines and solvents	Organics
19.	Dow Chemical	Midland, MI	Phenol	Phenols and acetic acid
20.	Hardwicke Chemical Co.	Elgin, SC	Intermediate and speciality organic chemicals	COD, color
21.	Crompton and Knowles Corp.	Gibralter, PA	Dyes	Dye, COD

TABLE 5-8. FULL-SCALE ACTIVATED CARBON SYSTEMS TREATING ORGANIC CHEMICAL WASTES

Company	Granular systems	Wastewater flow, gpd	Contaminants removed	Reactivation scheme	Comments
Allied Chemical Birmingham, AL	Hydrodarco 4000	3,000	Phenols	None	----
Dow Chemical Midland, MI	Wilco 718	145,000	Phenols	4% NaOH	Removes phenols from 18% brine solution for use in chlor/alkali plant. Reactivation solution recycled to phenol plant
East Coast Manufacturer NJ	Filtrasorb 400	58,000	Polyethers	Thermal	Discharges to municipal system
General Electric Pittsfield, ME	Filtrasorb 300	Batch treatment (varies with use)	Color	Thermal	Used for treating a variety of waste steam in-plant. On-stream December 1971
General Electric Selkirk, NY	Filtrasorb 300	300,000	Phenolics Toluene Color	Thermal	----
Hardwicke Chemicals Elgin, SC	Filtrasorb	20,000	Mixed organics	Thermal	Subscribes to Calgon Adsorption Service
Hercules Chemicals Hattiesburg, MS	Filtrasorb 400	3,200,000	COD Mixed organics Wood sugars	Thermal	Just completing start-up
Monsanto Anniston, AL	Filtrasorb 300	65,000	p-nitrophenol p-chlorobenzene	Chemical	Reactivation chemical with recovered product returned to process
Rhodia, Inc. Portland, OR	Filtrasorb 400	150,000	Chlorophenols	Thermal	----
Schenectady Chemicals Schenectady, NY	Filtrasorb 300	22,000	Phenols Resorcinol Xylol	Thermal	On stream March 1973
Stephan Chemical Co. Fieldsboro, NJ	Filtrasorb 300	15,000	Mixed organics associated with liquid detergent intermediates	Thermal	On stream June 1972
Stauffer Chemicals Skaneateles Falls, NY	Filtrasorb 300	8,000	COD from washout of batch equipment used to make mixed detergents and wash compounds	Expended carbon saved and shipped to central processing facility where a tank car load is accumulated	Treats segregated waste sidestream. Effluent then joins main waste stream

See footnote at end of table.

(continued)

TABLE 5-8 (continued)

Company	Granular systems	Wastewater flow, gpd	Contaminants removed	Reactivation scheme	Comments
Reichhold Chemicals Tuscaloosa, AL	Filtrasorb 300	500,000	Phenols, BOD, COD	Thermal	Treats concentrated waste resulting from extensive in-plant water use reduction. On-stream late 1972
Sherwin-Williams Chicago, IL	Nuchar WV-G, 12 × 40	65,000	p-cresol	10% NaOH	----
Vicksburg Chemical Vicksburg, MS	Hydrodarco 4000	10,000	Phenols	NaOH	----
Ashland Chemicals Great Meadows, NJ	Hydrodarco[a]	140,000	Color, COD	None	Biological treatment with 65 ppm of carbon added to influent
Dow Chemical Midland, MI	Nuchar[a]	14,000,000	Mixed organics	None	Biological treatment with carbon added to influent
Koppers Chemical Follunsbee, WV	Nuchar[a]	20,000	Phenolics	None	Used when biological treatment efficiency drops

[a] Powdered system.

TABLE 5-9. INDUSTRIAL WASTEWATER TREATMENT GRANULAR ACTIVATED CARBON INSTALLATIONS

Industry and location	Installation date	Design Flow Rate (1,000 gpd)	Organic Contaminants	Pretreatment	Adsorption System		
					Contact Time (min)	Adsorber type	Carbon reactivation
1. Carpet Mill British Columbia	6/73	50	Dyes	Screens	-	Moving bed	None
2. Textile Mill Virginia	7/70	60	Dyes	Filtration	57	Moving bed	None
3. Oil Refinery California	3/71	4,200	COD	Equalization Oil Flotation	60	Gravity beds in parallel	Multiple hearth furnace
4. Oil Refinery Pennsylvania	3/73	2,200	BOD	Equalization Oil Flotation Filtration	-	Moving bed	Multiple hearth furnace
5. Detergent New Jersey	6/72	15	Xylene Alcohols TOC	None	540	Downflow beds in series	Multiple hearth furnace
6. Chemicals Alabama	11/72	500	Phenolics Resin Intermediates	Chemical Clarification	173	Moving beds	Multiple hearth furnace
7. Resins New York	3/73	22	Xylene Phenolics Resorcinol	Chemical Clarification	30	Downflow beds in series	Rotary kiln
8. Herbicide Oregon	11/69	150	Chlorophenols Cresol	None	105	Upflow beds in series	Multiple hearth furnace
9. Chemicals New York	3/69	15	Phenol COD	Equalization	200	Downflow beds in series	None
10. Chemicals Texas	11/71	1,500	Nitrated aromatics	Activated sludge Filtration	40	Moving beds	Rotary kiln
11. Chemicals New Jersey		100	Polyols	Equalization Clarification		Moving bed	Multiple hearth furnace
12. Explosives Switzerland	3/72	5	Nitrated phenols	Equalization	150	Downflow beds in series	None

(continued)

TABLE 5-9 (continued)

Industry location	Installation date	Design Flow Rate (1,000 gpd)	Organic Contaminants	Pretreatment	Adsorption System		
					Contact Time (min)	Adsorber type	Carbon reactivation
13. Pharmaceuticals Switzerland	10/72	25	Phenol	Equalization pH adjusted settling	90	Downflow beds in series	None
14. Insecticide England	1962	-	Chlorophenol	Equalization Clarification	-	Downflow beds in series	Rotary kiln
15. Wood Chemicals Mississippi	8/73	3,000	TOC	pH adjustment Flotation Filtration	50	Moving beds	Multiple hearth furnace
16. Dyestuffs Pennsylvania	8/73	1,500	Color TOC	Equalization Clarification Filtration	50	Moving beds	Multiple hearth furnace

The variety of possible carbon adsorption systems may lead to unit costs (e.g., dollars/1,000 gallons) that vary over two orders of magnitude. This report does not attempt to cover all possible system designs or to discuss the economic effects of all design variables. The reader is referred to EPA (1973) and Loven and Pieroni (1969) for more detailed information on carbon treatment economics.

Since thermal reactivation is the most widely used method of carbon reactivation, we will examine briefly the major variables that affect capital and operating costs for this type of system. These costs are functions primarily of two variables:

- Carbon reactivation rate, usually expressed as pounds of carbon reactivated per volume of liquid treated; and
- Superficial liquid retention time, the time that the liquid will take to fill the volume of the carbon bed. This is a function of the liquid flow rate and the carbon volume.

These two primary variables are related for a specific system through an "operating line"--a curve that is convex toward the liquid retention time axis in a plot of liquid retention time vs. carbon exhaustion rate. This operating line is determined in laboratory adsorption isotherm and columm kinetics studies.

The position of this operating line is a characteristic of the particular waste stream-carbon system, and it depends on (among other factors) the effluent quality desired and the system configuration. For example, if a lower concentration effluent is required, the minimum exhaustion rate and retention time (in the adsorber) increase, and the operating line moves further from the origin. The choice of a countercurrent moving-bed contactor results in an operating line closer to the origin of the plot compared to a single fixed-bed unit which makes less efficient use of the carbon. Once this operating line is established, the optimum or least-cost design may be selected. The adsorption and reactivation portions of the system are then sized from this optimum retention time-exhaustion rate.

The total capital cost of the system is essentially set by the volume of the carbon beds and the size of the reactivation furnace. The annual operating costs are determined mainly by the carbon exhaustion rate because this factor affects the utility demand (fuel, steam, and electricity use) and the amount of makeup carbon to required replaced carbon losses. The carbon losses are the result of some burning away of the carbon during reactivation and the mechanical breakage or attrition of the carbon granules during transporting operations between the process units.

Costs for thermally reactivating carbon increase rapidly as the volume reactivated falls below 1,000 lb/day and at some point reactivation becomes more expensive than carbon replacement in a throw-away system. For high volume systems reactivating more than 1,000 lb of carbon per day, regeneration costs are about $0.10 to $0.15/lb (Berkowitz et al. 1978) and do not decrease substantially for larger systems. In adsorption systems treating wastes at concentration above 1,000 ppm, capital costs for thermal reactivation can be 45 to 50 percent of the total capital costs; and these increase as adsorbate concentration in the influent increases.

5.3.2.2 Example Case: Carbon Adsorption--

5.3.2.2.1 WET stream--The WET Model hazardous waste streams were examined and individual streams considered to be candidates for liquid phase carbon adsorption were identified. Waste stream 02.02.14 was selected as an example to show a typical carbon adsorption system design, associated material balances, and treatment economics.

This stream with a nominal rate of 426,000 kg/day (17,750 kg/h) contains benzene, toluene, and phenol at concentrations ranging between 3,000 and 5,000 ppm. Although these concentrations are on the upper range of the concentrations currently being treated in commercial practice, GAC has been shown to be effective for these constituents at these levels. The composition of WET stream 02.02.14 is given in Table 5-10.

5.3.2.2.2 Process flowsheet--The process flowsheet for carbon adsorption pretreatment of the above waste stream is shown in Figure 5-7. The process design and configuration shown includes waste stream preconditioning, moving-bed adsorption, thermal reactivation, and furnace offgas cleaning units. The preconditioning system is designed to remove suspended solids to below 50 ppm and to allow pH adjustment of the waste influent for maximum adsorption efficiency of the carbon.

TABLE 5-10. COMPOSITION OF WET STREAM 02.02.14

Component	Mass fraction	Flow rate kg/hr
Benzene	0.005	88.8
Phenol	0.003	53.3
Toluene	0.004	71.0
Solids	0.01	177.5
Water	0.98	17,359.5
Total	1.002	17,750.1

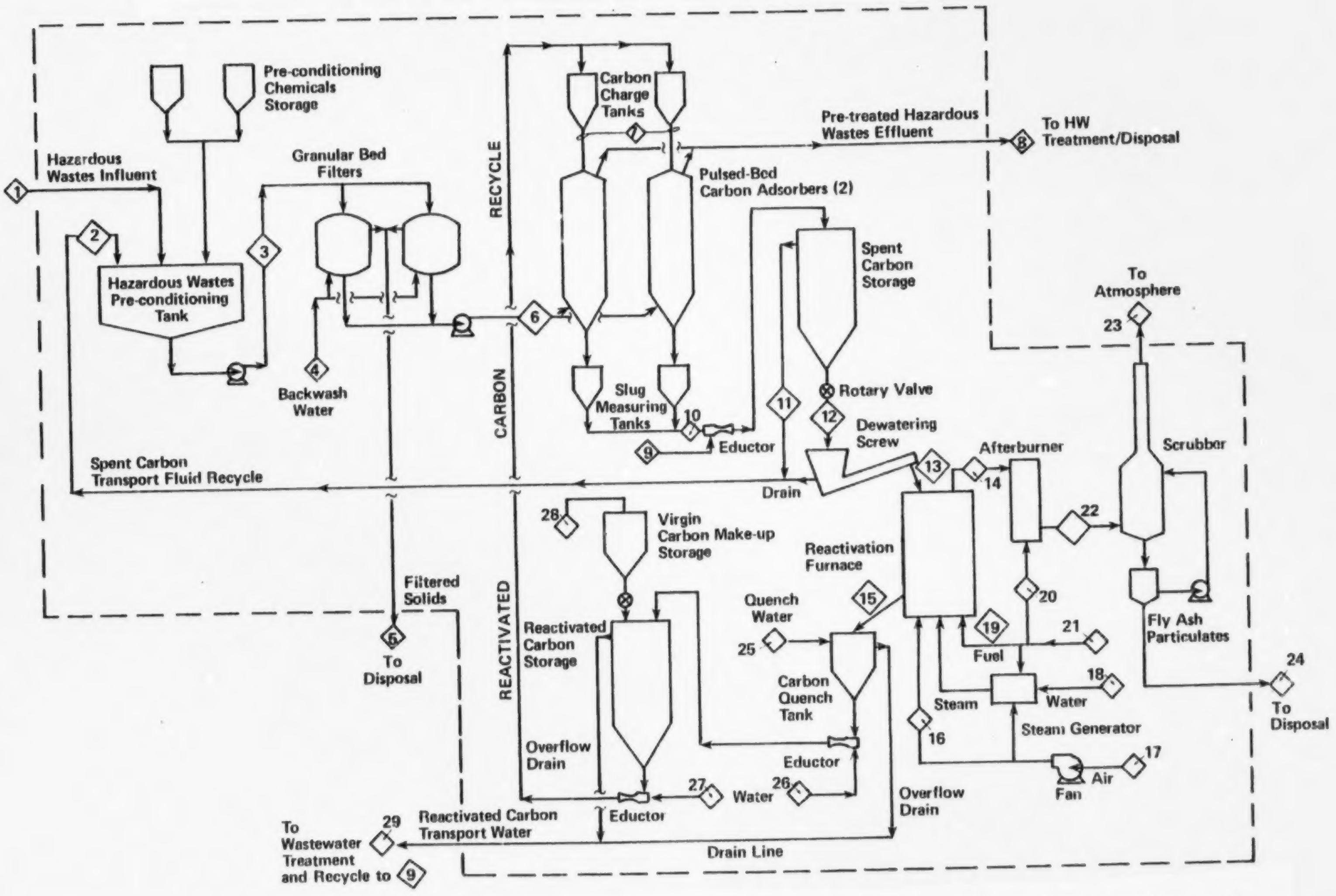

Pre-conditioning Chemicals Storage
Hazardous Wastes Influent
1
2
Hazardous Wastes Pre-conditioning Tank
3
Granular Bed Filters
4
Backwash Water
RECYCLE
CARBON
REACTIVATED
6
Carbon Charge Tanks
7
Pre-treated Hazardous Wastes Effluent
8
To HW Treatment/Disposal
Pulsed-Bed Carbon Adsorbers (2)
Spent Carbon Storage
Slug Measuring Tanks
10
9
Eductor
11
Rotary Valve
12
Dewatering Screw
Spent Carbon Transport Fluid Recycle
Drain
13
14
Afterburner
22
Scrubber
To Atmosphere
23
28
Virgin Carbon Make-up Storage
Reactivation Furnace
Filtered Solids
5
To Disposal
Reactivated Carbon Storage
Quench Water
25
15
Carbon Quench Tank
19
20
21
Fuel
18
Water
Steam
Steam Generator
16
17
Air
Fan
Fly Ash Particulates
24
To Disposal
Overflow Drain
Eductor
27
Water
26
Overflow Drain
Eductor
To Wastewater Treatment and Recycle to 9
29
Reactivated Carbon Transport Water
Drain Line

Figure 5-7. Process flow sheet for carbon adsorption pretreatment to remove volatile constituents from hazardous waste.

Stream Number	Stream Components (kg/h)											
	Toluene	Phenol	Benzene	Solids	Water	Activated Carbon	Carbon Dioxide	Nitrogen	Oxygen	Methane (fuel)	Ash	Total
1	71	53	89	178	17,360	–	–	–	–	–	–	17,750
2	–	–	–	–	7,385	–	–	–	–	–	–	7,385
3	71	53	89	178	24,745	–	–	–	–	–	–	25,136
4	–	–	–	–	1,557	–	–	–	–	–	–	1,557
5	–	–	–	177	1,557	–	–	–	–	–	–	1,734
6	71	53	89	1	24,745	–	–	–	–	–	–	24,959
7	–	–	–	–	1,657	710	–	–	–	–	–	2,367
8	–	–	–	<1	24,745	–	–	–	–	–	–	24,745
9	–	–	–	–	6,651	–	–	–	–	–	–	6,651
10	71	53	89	–	1,657	710	–	–	–	–	–	2,580
11	–	–	–	–	6,154	–	–	–	–	–	–	6,154
12	71	53	89	–	2,154	710	–	–	–	–	–	3,077
13	71	53	89	–	923	710	–	–	–	–	–	1,846
14	–	–	–	–	1,346	–	790	2,580	55	–	17	4,788
15	–	–	–	–	–	667	–	–	–	–	–	667
16	–	–	–	–	–	–	–	2,580	686	–	–	3,266
17	–	–	–	–	–	–	–	9,463	2,516	–	–	11,979
18	–	–	–	–	710	–	–	–	–	–	–	710
19	–	–	–	–	–	–	–	–	–	158	–	158
20	–	–	–	–	–	–	–	–	–	127	–	127
21	–	–	–	–	–	–	–	–	–	331	–	331
22	–	–	–	–	1,631	–	1,138	4,485	55	–	17	7,326
23	–	–	–	–	1,631	–	1,138	4,485	55	–	–	7,309
24	–	–	–	–	–	–	–	–	–	–	17	17
25	–	–	–	–	1,945	–	–	–	–	–	–	1,945
26	–	–	–	–	4,007	–	–	–	–	–	–	4,007
27	–	–	–	–	4,007	–	–	–	–	–	–	4,007
28	–	–	–	–	–	43	–	–	–	–	–	43
29	–	–	–	–	9,000	–	–	–	–	–	–	9,000

Figure 5-7 (continued).

Two countercurrent flow, moving-bed carbon contactors, which provide the most efficient utilization of the carbon, make up the adsorption system. The reactivation furnace is a fluidized-bed type. Although historically, multihearth furnaces have been used for carbon reactivation, they suffer from mechanical problems and hearth failures. Recently, several fluidized beds have been installed at municipal water treatment and industrial wastewater treatment facilities, and they have been found to be a viable alternative to the multihearth furnace.

The material balance for the example pretreatment is shown in the tabular portion of Figure 5-7. Although the material balance indicates essentially 100 percent removal of the three organics, in actual practice the waste effluent from the carbon contactors (stream No. 8) may contain these constituents at concentrations of several ppm.

As noted above, key design variables for carbon adsorption systems are the carbon retention time in the adsorber and the carbon exhaustion rate. In addition, for the thermal reactivation case, control of the furnace conditions (residence time, temperature, and process gas composition) are needed to minimize carbon burnoff and to insure adequate restoration of carbon capacity.

The major process uncertainties in carbon adsorption are: (1) the equilibrium capacity of the carbon for the three organics in a multicomponent aqueous solution of this particular composition, (2) the adsorber residence (retention) time, and (3) the carbon recirculation rate. For the case here, we assumed a carbon loading of 0.3 kg adsorbate/kg carbon and a minimum adsorber residence time of 30 minutes. Also, to size the reactivation furnace, a furnace residence time of 30 minutes was assumed. These assumptions are consistent with the ranges used in current practice.

5.3.2.2.3 Economics--The capital and operating costs for the above example case were based on 24 h/day, 330 day/yr operation, an adsorber design capacity of 200,000 gal/day (126 percent of waste stream rate including recycle streams to the adsorber), and reactivation furnace throughput rate of 25,500 kg carbon/day. The capital costs of the major components of the carbon treatment system including support equipment, installation, engineering, legal, financing, and administrative costs are presented in Table 5-11.

TABLE 5-11. CAPITAL AND OPERATING COSTS FOR CARBON ADSORPTION PRETREATMENT WITH THERMAL REACTIVATION OF THE CARBON FOR WET MODEL STREAM 02.02.14

Capital Costs	
Influent pump station	21,000
Carbon adsorption system (2 pulsed bed contactors)	181,000
Carbon regeneration system (fluidized bed furnace)	1,925,000
Carbon inventory (150,000 lb @ $0.85/lb)	128,000
Construction costs[a]	925,000
Total Installed Cost	$3,180,000
Annualized Operating Cost	
Operating labor (36,000 man-hours @ $15/m-h)	540,000
Maintenance (5% of capital cost)	159,000
Electricity (824,000 kWh @ $0.05/kWh)	41,200
Steam (13,680,000 lb @ $4/1,000 lb)	54,700
Fuel (1,430,000 therms @ $0.59/therm)	840,000
Water (20,800,000 gal @ $0.40/1,000 gal)	8,300
Carbon makeup (829,000 lb @ $0.85/lb)	704,700
Taxes, insurance, administration (4% of capital cost)	127,200
Capital recovery (16.3%; 10% over 10 years)	518,300
Total Operating Costs	$2,993,400
Product Recovery Credit	0
Net Operating Costs	$2,993,400
Waste treated (kg/yr)	155,490,000
Total volatiles removed (kg/yr)	1,865,880
Unit treatment cost ($/kg waste treated)	0.019 $/kg
($/kg volatiles removed)	1.60 $/kg

[a] Construction fee (10%), contingency (15%), engineering (15%), startup (1%).

The annual operating costs for the system are also included in Table 5-11. The major operating costs include: labor, electricity, fuel (natural gas), maintenance materials, and carbon makeup.

5.3.2.3 Advantages and Disadvantages--

The major advantages of carbon pretreatment are:

- It is a mature technology in commercial use for waste treatment applications.
- Carbon adsorption can handle a broad range of organic constituents and concentrations.

The disadvantages of carbon pretreatment include:

- Carbon adsorption treatment, especially with thermal reactivation, is a complex and labor-intensive operation.
- Carbon adsorption has substantial operating costs.

5.3.2.4 Recommendations--

The following recommendations are offered regarding the assessment of carbon adsorption for pretreatment of hazardous wastes:

1. Conduct laboratory isotherm and column studies on actual waste streams to determine process operating lines for preliminary feasibility and cost analysis.
2. Conduct field tests on existing commercial carbon systems.

5.3.3 Resin Adsorption

5.3.3.1 State of the Art--

Resin adsorption is a treatment process that is very similar to carbon adsorption, and much of the discussion in Section 5.3.2 is directly applicable here. Since the nature of the resin and carbon adsorption processes are similar, the two processes may be competitive in some applications.

One significant difference between resin and carbon adsorption is that resins are always chemically regenerated by caustic or organic solvents while carbons, because the adsorption forces are stronger, are usually thermally regenerated thus eliminating the possibility of material recovery. On the other hand, resins generally have lower adsorption capacities than carbons. Also, resins are more solute specific than are carbon adsorbers.

Although resin adsorption involves the same operating principles and to a substantial extent the same processing scheme and equipment (except for regeneration), resin adsorption is not as mature as carbon adsorption, and it is not in widespread commercial use. While the investigation of synthetic resins dates back to the mid-1940's, the technique has only been in commercial use in the last decade. The use of resin adsorbents is increasing, however, as their capabilities are demonstrated and as wider varieties of resins are manufactured for separation purposes.

5.3.3.1.1 Process description--

Principles of Operation--Resin adsorption treatment of waste streams involves two basic process steps: (1) contacting the liquid waste influent with the resin and allowing the resin to adsorb the solute(s) from the solution; and (2) subsequently regenerating the resin by removing the adsorbed chemicals with a wash of the proper solvent. In those cases where expensive organic solvents are used for resin regeneration, a third process step--solvent and solute recovery--is used to allow solvent recycle. Typically, distillation is used in this third step to separate the solvent and adsorbate.

The chemical nature of commercially available resins can vary widely; it can also be more readily controlled than activated carbon. Perhaps the most important variable in this respect is the degree of hydrophilicity. The adsorption of a nonpolar molecule onto a hydrophobic resin such as a styrene-divinylbenzene-based resin results primarily from van der Waal's forces. In other cases, different interactions such as dipole-dipole interaction and hydrogen bonding may dominate. In a few cases, an ion exchange mechanism may be involved. The adsorption of alkylbenzene sulfonate from an aqueous solution on weakly basic resins as phenol-formaldehyde-amine based resin is an example of this latter interaction.

Although the degree of resin adsorption of a particular solute cannot be predicted with any degree of certainty, in general, hydrophobic nonpolar molecules or molecules possessing nonpolar portions are attracted to hydrophobic surfaces and hydrophilic polar molecules are attracted to hydrophilic surfaces.

Basic Process Configuration--Resin adsorbents are used in much the same way as carbon and in some situations compete directly with carbon. A typical resin adsorption system for treating low-volume waste streams consists of two fixed beds of resin. One bed is on-stream adsorbing solute(s) from the waste stream while the other is off-stream undergoing regeneration. In situations where the adsorption time is much longer than the regeneration time, one adsorbent column and a hold-up storage tank could suffice. Large-volume waste streams may include multiple columns and a solvent-solute separation system for recovery of the solute(s) and recycle of the solvent.

The adsorption bed is usually fed downflow at flow rates in the range of 0.25 to 2 gal/min per cubic foot of resin which is the equivalent of 2 to 16 bed volumes/h. At these flow rates, the resin contact time is in the range of 3 to 30 minutes and the linear flow rates in the range of 1 to 10 gal/min/ft^2. Adsorption is stopped when the bed is fully loaded (i.e., effluent concentration equals influent concentration) or when the effluent concentration reaches a prescribed level.

Regeneration of the resin bed is performed in situ with basic, acidic, and salt solutions or regenerable nonaqueous solvents most commonly used. Basic solutions may be used to remove weakly acidic solutes and acidic solutions to remove weakly basic solutes; hot water and steam can be used to remove volatile solutes; and methanol and acetone are often used to remove nonionic organic solutes. In some cases a prerinse and/or postrinse is required. As a rule, about three bed volumes of regenerant are required for resin regeneration although as little as one-and-a-half bed volumes may be sufficient in certain instances.

Solvent regeneration with solute recovery is generally part of the treatment system unless (1) the solute-laden solvent can be used directly as a feed stream at some point in the industrial process, or (2) the cost of the solvent is low enough that it may be disposed after a single use. Solvent recovery, usually by distillation, is the most common method when organic solvents are used. Distillation allows recovery of the solute for sale if it is desired.

5.3.3.1.2 Process operation--

Applicable Feed Stream--Like carbon adsorption systems, the feed stream to a resin adsorption system must be a single liquid phase. In most cases, this stream is an aqueous solution; but there is no technical reason to preclude a nonaqueous stream provided it does not chemically or physically harm the resin. The following guidelines should be considered when selecting a waste for resin adsorption treatment:

- Suspended solids should be less than 50 ppm and may, in some cases, have to be below 10 ppm to prevent bed clogging. Prefiltering the waste stream is a possible option to allow treatment of streams with higher suspended solids.
- Resin adsorption is generally pH dependent and therefore requires pH control of the waste stream. Some resins have operated successfully at pH's as low as 1 to 2 and as high as 11 to 12.
- Temperature is an important variable in resin adsorption; low temperatures generally favor adsorption and high temperatures favor regeneration. The operating temperature range for resin adsorption, is more limited than that for carbon adsorption. However, resins have been used in applications where the influent temperature was as high as 80° C.
- High levels of dissolved solids, particularly inorganic salts, do not interfere with resin adsorption of organic solutes. In fact, some resin applications suggest that the organic solutes are more easily removed from solutions with high concentrations of dissolved salts than from salt-free solutions. But, in some high salt solutions, prerinse of the resin adsorbent is necessary before it is regenerated.
- Technically, the concentration of organic solute(s) that can be treated by resin adsorption is not bounded. Phenol concentrations as high as 8 percent (weight) have been successfully handled. Similarly low concentrations have been treated as well. But, as with carbon, resin adsorption is generally more efficient at higher concentrations.
- Chemicals such as strong oxidants that would chemically attack the resin must be kept out of the influent streams.

Process Emissions and Wastes--Output streams from resin adsorption systems vary from system to system; but basically they include a treated effluent stream, washing effluent streams, and a regenerant effluent stream.

The treated waste effluent stream will contain those materials not adsorbed by the resin and possibly some very low concentrations of the adsorbed solutes, depending on the removal efficiency of the system under the operating conditions.

Prerinse and/or postrinse of the resin bed with water is often required and will yield an aqueous effluent containing organic and/or inorganic solutes depending on the system and application. Treatment of these wash effluents is generally required either for pollutant removal before discharge or for solvent recovery.

Each bed regeneration will produce approximately three bed volumes of solute-laden regenerant effluent. This effluent may:

- be further treated for both solvent and solute recovery, in which case no significant effluents are generated for disposal
- be treated only for solvent recovery, e.g., by distillation, in which case a concentrated effluent is produced for disposal
- be directly disposed of after any necessary treatment, e.g., caustic regeneration with 2-4 percent NaOH may be treated by evaporation followed by incineration.

Removal Efficiency--Like carbon adsorption systems, resin adsorption systems can be designed and operated to achieve virtually any degree of removal efficiency. This flexibility is essentially achieved by controlling influent flow rate, resin contact time, influent pH, and frequency of regeneration. The capital and operating costs, however, increase dramatically as the desired removal efficiency approaches 100 percent. Typically, commercial resin adsorption systems operate with removal efficiencies well over 99 percent. For example, a resin-treated waste effluent with phenol concentrations below 10 ppm has been produced from an influent containing 5% phenol, a removal efficiency of better than 99.98 percent (Berkowitz et al. 1978). Similarly, influents containing solutes at several ppm levels have been treated to yield an effluent with residual solute concentrations at the ppb level.

State of Recovered Volatiles--Resin adsorption's major advantage over carbon adsorption is its greater ability to recover solute(s) from the waste influent. In fact, when solute recovery is not the objective, usually carbon adsorption systems are used. Distillation is most frequently used to recover the solute(s) in a resin treatment system; in this case, the volatile organics may be recovered at a purity suitable for resale.

5.3.3.1.3 Existing sites--There is little publicly available information on current or proposed industrial applications of resin adsorption systems. Two large systems have been in operation in Sweden (Anderson et al. 1973; Anderson et al. 1974) and in Japan to remove color pollutants (lignin derivatives) from paper mill bleach plant effluents. Some operational resin adsorption units in are used to remove color in water supply systems; others are used to deodorize sugar, glycerol, wines, milk whey, pharmaceuticals and similar products.

An Indiana plant installed a resin system in 1975 to recover phenol from a waste stream and a coal liquefaction plant in West Virginia installed a resin adsorption system to remove phenol and high molecular weight polycyclic hydrocarbons from a 10 gal/min waste stream (Berkowitz et al. 1978).

5.3.3.1.4 Process economics--The process economics of resin adsorption as well as the major design and operating variables that affect process economics are essentially the same as those for carbon adsorption. The reader is referred to Section 5.3.2.1.4 for further details.

The major difference between capital costs for a resin and carbon adsorption system is the difference in the cost of the adsorbent and the amount of adsorbent required to remove the same quantity of solute. Resin adsorbents are substantially more expensive than activated carbon adsorbents and generally have a lower capacity; therefore, the cost of the adsorbent is a larger percentage of the capital costs in a resin system.

Because resin adsorption systems are typically used where solute recovery is an objective, these systems can generally offset a significant portion of their operating cost by the sale of the recovered product.

5.3.3.2 Example Case: Resin Adsorption--

5.3.3.2.1 WET stream--The WET Model hazardous waste streams were examined to determine those streams that appear suitable for resin adsorption treatment. Waste stream 02.02.16 was selected for this example case.

This particular stream is characteristic of decanter wastes from phenol production by cumene hydroperoxide cleavage. Specifically, this is an aqueous stream with a nominal flow rate of 350,000 kg/day (14,580 kg/h) and contains approximately 0.02 kg phenol/kg solution and 1 percent suspended solids.

5.3.3.2.2 Process flowsheet--The resin adsorption system, shown in Figure 5-8, includes solvent reactivation of the spent resin, recovery/recycle of the solvent, and recovery of the organic waste by distillation. The fixed-bed resin contactors are designed to operate cyclically between adsorption and reactivation (desorption) modes and to produce an effluent containing less than 10 ppm phenol. At any given time, half of the contactors, which are sized for 12-hour operating cycles, are being reactivated in situ by solvent (acetone) washing, followed by a water rinse prior to returning the contactors to the adsorption operating mode. Three distillation columns are used to recover the solvent (acetone) for reuse and to recover the waste (phenol). In addition, to optimize distillation operations for variable phenol concentrations in the waste influent, a flow-controlled stream containing phenol from the resin regeneration system is recycled to the on-stream resin adsorbers. The flow rate of this stream may be adjusted according to the phenol concentration in the waste influent to provide a more constant resin loading.

The material balance for the example process is also included in Figure 5-8. With the internal phenol recycle streams from the resin regeneration operation to the on-stream adsorbers, the actual flow rate to the resin adsorbers is higher than the waste influent rate.

Like the carbon adsorption systems discussed earlier, the key design variables for resin adsorption systems are the resin retention time in the adsorber and the resin exhaustion rate. High retention times increase the size of the adsorber and high exhaustion rates increase the frequency of resin regeneration.

The major process uncertainties are: (1) equilibrium capacity of the resin in the presence of any other unidentified organics in the waste stream, (2) the adsorber residence (retention) time, and (3) the residual resin adsorption capacity (working capacity) after regeneration.

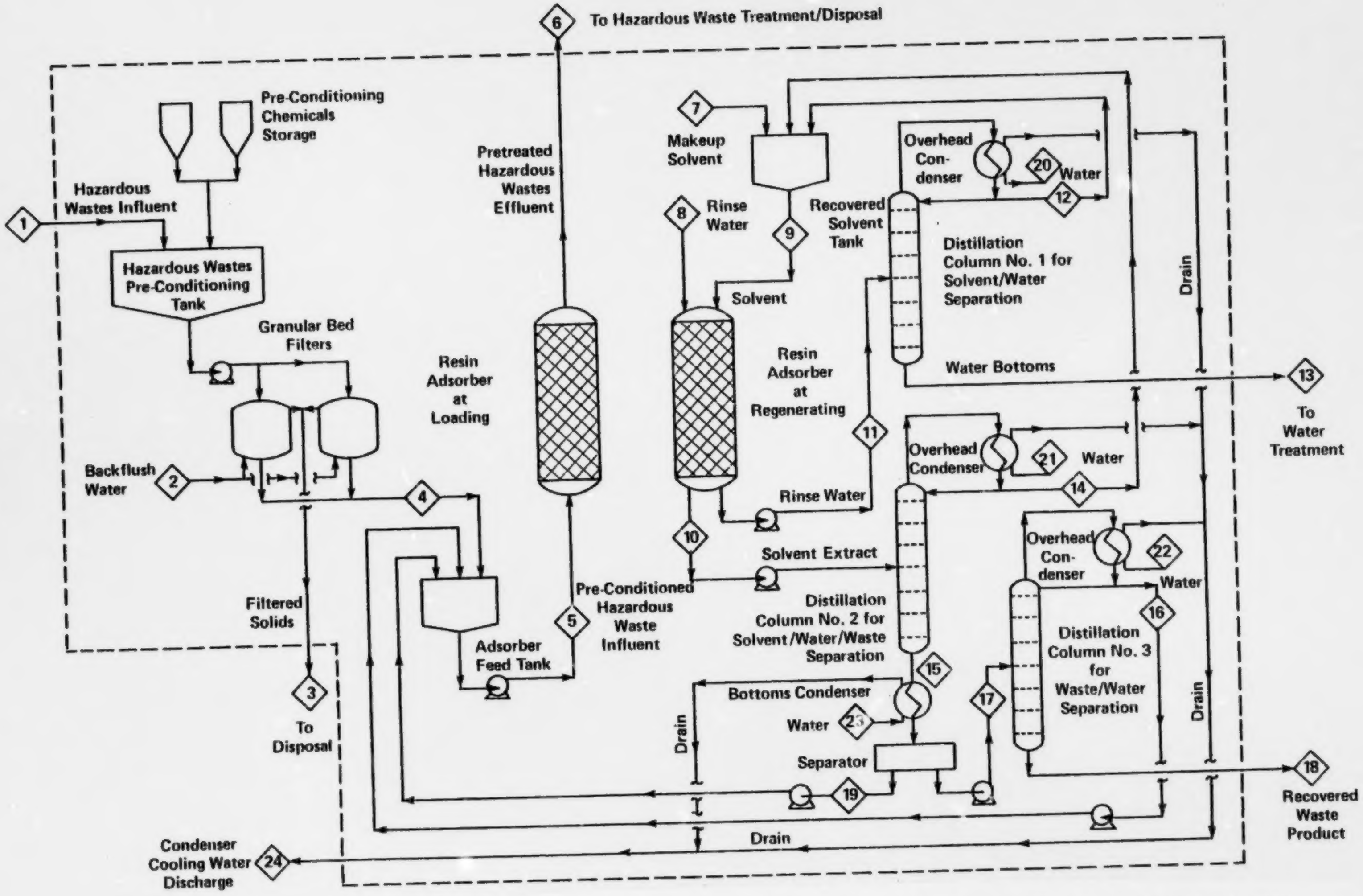

To Hazardous Waste Treatment/Disposal
6
Pre-Conditioning Chemicals Storage
Hazardous Wastes Influent
1
Hazardous Wastes Pre-Conditioning Tank
Granular Bed Filters
Backflush Water
2
Filtered Solids
3
To Disposal
4
Resin Adsorber at Loading
Pretreated Hazardous Wastes Effluent
Adsorber Feed Tank
5
Pre-Conditioned Hazardous Waste Influent
7
Makeup Solvent
8
Rinse Water
9
Solvent
Resin Adsorber at Regenerating
10
Rinse Water
11
Solvent Extract
Recovered Solvent Tank
Overhead Con-denser
20
Water
12
Distillation Column No. 1 for Solvent/Water Separation
Water Bottoms
Drain
13
To Water Treatment
Overhead Condenser
21
Water
14
Distillation Column No. 2 for Solvent/Water/Waste Separation
15
Bottoms Condenser
Water
23
Drain
Separator
19
17
Overhead Con-denser
22
Water
16
Distillation Column No. 3 for Waste/Water Separation
Drain
18
Recovered Waste Product
Drain
Condenser Cooling Water Discharge
24

Figure 5-8. Process flow sheet for resin adsorption pretreatment to remove volatile constituents from hazardous waste.

5-8

	Stream Components (kg/h)					
Stream Number	Phenol	Nonwater (balance)	Acetone (regenerated)	Water	Solids	Total
1	292	729	–	13,416	146	14,583
2	–	–	–	921	–	921
3	3	8	–	910	145	1,066
4	289	721	–	13,427	1	14,438
5	546	721	–	15,054	1	16,322
6	–	721	–	15,054	1	15,776
7	–	–	5	–	–	5
8	–	–	–	3,130	–	3,130
9	–	–	4,076	305	–	4,356
10	546	–	2,139	1,749	–	4,558
11	–	–	1,937	1,686	–	3,623
12	–	–	1,933	59	–	1,992
13	–	–	54	1,637	–	1,631
14	–	–	2,139	112	–	2,251
15	546	–	–	1,637	–	2,183
16	148	–	–	177	–	325
17	437	–	–	187	–	624
18	289	–	–	–	–	289
19	109	–	–	1,450	–	1,559
20	–	–	–	398,400	–	398,400
21	–	–	–	450,200	–	450,200
22	–	–	–	65,000	–	65,000
23	–	–	–	32,750	–	32,750
24	–	–	–	946,350	–	946,350

Figure 5-8 (continued).

5.3.3.2.3 Economics--The estimated capital and operating costs for the above example case are shown in Table 5-12. These costs are based on 24 h/day, 365 day/yr operation. On this basis, the resin adsorption system would recover approximately 2,558,000 kg phenol/yr. The amount of waste treated would be 127,750,000 kg/yr.

The total capital cost is estimated to be $3,214,800 (January 1983 dollars). Discounting the capital costs at 10 percent over 10 years results in a total annualized cost of $1,348,100/yr. If the recovered phenol is sold at $0.22/kg, a credit against operation costs of $562,700/yr may be realized. Based on net annualized costs, the unit treatment cost would be $0.00615/kg waste treated or $0.031/kg phenol removed.

5.3.3.3 Advantages and Disadvantages--

The major advantages of resin pretreatment are:

- It is an established technology in commercial use for waste treatment applications.
- Resins may be more selective and specific to particular solutes than carbon.
- Greater control of the resin adsorbent's chemical/physical properties is possible compared to carbon adsorbents.

The major disadvantages are:

- Resin adsorbents are substantially more expensive than carbons.
- Resins generally have lower adsorption capacities than carbons.
- Often the entire resin inventory becomes exhausted, i.e., it cannot be adequately regenerated, and must be replaced with fresh resin.

5.3.3.4 Recommendations--

The following recommendations regarding the assessment of resin adsorption for pretreatment of hazardous wastes are offered.

- Conduct laboratory isotherm and column studies on actual waste streams to determine process operating lines for preliminary feasibility and cost analysis.
- Conduct field tests on existing commercial resin adsorption systems.
- Compile a data base on new resins that are becoming available.

TABLE 5-12. CAPITAL AND OPERATING COSTS FOR RESIN ADSORPTION PRETREATMENT WITH SOLVENT AND WASTE RECOVERY FOR WET MODEL STREAM 02.02.16

Capital Costs	
Resin adsorption columns (4 required)	$240,000
Solvent recovery system	600,000
Resin inventory (7,200 ft^3 @ $200/ft^3)	1,440,000
Construction cost[a]	934,800
Total capital costs	$3,214,800
Annualized Operating Costs	
Operating labor (8,400 man-hours @ $15/m-h)	$126,000
Maintenance (5% of capital cost)	160,700
Electricity (246,000 kWh @ $0.05/kWh)	12,300
Steam (69,000,000 lb @ $4/1,000 lb)	276,000
Cooling water (1,980,000,000 gal @ $0.03/1,000 gal)	59,400
Make-up water (20,000,000 gal @ $0.4/1,000 gal)	8,000
Resin replacement (200 ft^3 @ $200/ft^3)	40,000
Solvent (87,100 lb @ $0.15/lb)	13,100
Taxes, insurance, administration (4% of capital cost)	128,600
Capital recovery (16.3%; 10% over 10 years)	524,000
Total Operating Costs	$1,348,100
Product Recovery Credit (5,627,000 lb @ $0.10/lb)	562,700
Net Operating Costs	$785,400
Waste treated (kg/yr)	127,750,000
Total volatiles removed (kg/yr) (99% removal efficiency)	2,558,000
Unit treatment cost ($/kg waste treated)	0.0062 $/kg
($/kg volatiles removed)	0.31 $/kg

[a] Construction fee (10%), contingency (15%), engineering (15%), startup (1%).

5.3.4 Air Stripping/Adsorption

The two previous adsorption methods of waste treatment bring the waste stream into direct contact with the adsorbent to remove the volatile organics as well as other high molecular weight constituents. Some waste streams may be suitable for adsorption treatment, but direct contact between adsorbent and waste stream may not be efficient or cost effective. In these situations, chemical process operations such as air stripping or evaporation can be used. These two processes separate the volatile organics from the liquid waste stream and place them in a gas or vapor stream that can be treated with an adsorbent to capture the organic vapors. Again, like liquid phase adsorption, gas/vapor phase adsorption is a well established process technology. Sections 5.3.4 and 5.3.5 focus on the combined treatment processes of air stripping/adsorption and evaporation/adsorption, respectively, for the treatment of hazardous wastes to control the release of volatile organics.

5.3.4.1 State of the Art--

5.3.4.1.1 Process description--

Principles of Operation--Each constituent in the waste stream exerts a vapor pressure that is characteristic of that constituent and its interaction with the solvent (major component). At low solute concentrations the relationship between the concentration of the solute in the liquid phase (waste stream) and its equilibrium vapor pressure is described by Henry's law. A large Henry's law constant indicates that the solute exerts a high vapor pressure in the vapor phase in contact with the solution.

In cases where the partitioning of the solute between the liquid and vapor phase is high, i.e., a high Henry's law constant, the solute may be removed from the liquid phase by maintaining the vapor pressure of the solute below its equilibrium level. One way of keeping the solute's partial pressure in the vapor below its equilibrium level is to continuously sweep the surface of the liquid phase with air. The efficiency of this method in removing the solute increases as Henry's law constant increases.

Air stripping removal reverses the absorption process that is widely used to remove constituents from the gas phase, e.g., in air pollution control. Like absorption, air stripping may be carried out in packed or bubble tray columns where the liquid phase enters the top of the column and flows downward countercurrently to the upward flowing gas phase.

In cases where there are no chemical interactions between the solute and the solvent or other solutes, Henry's law constant generally increases with temperature. Therefore, improved air stripping efficiencies may be obtained by operating at higher temperatures.

The solute must then be removed from the gas phase to prevent it from entering the atmosphere. Adsorption onto a porous solid is one method of removing the solute from the gas phase. The solute may then be desorbed from the adsorbent in a more concentrated state and recovered or incinerated.

Basic Process Configuration--The air stripping/adsorption waste treatment process basically consists of three operational steps: (1) air stripping (liquid-air contacting), (2) adsorption (air-solid contacting), and (3) adsorbent regeneration/adsorbate recovery.

The air stripping of the waste stream may be carried out in packed or bubble tray (bubble cap or perforated plate) columns. In waste treatment the packed columns are more frequently used because of their lower cost and reduced tendency for liquid foaming. The height of the packed column and the gas-liquid flow ratio are largely determined by Henry's law constant and the degree of solute removal required.

The solute-laden air effluent from the stripping column is then passed through an adsorbent column. Fixed beds of activated carbon are the most widely used adsorption method for removing organics from the vapor phase. The cleaned air leaving the adsorbent bed is then vented to the atmosphere. This air leaving the adsorber typically contains lower organic concentrations than the ambient air.

Multiple adsorbent beds are used in the adsorption step; a portion of the beds are on-stream (adsorbing) while the remaining ones are off-stream (desorbing). This is analogous to the two-cycle operation described earlier for liquid phase carbon and resin adsorption. Although only two adsorbent beds are required, frequently more beds are used to allow longer desorption time. Since the kinetics of gas phase desorption are usually slower than adsorption, the longer desorption times are necessary to achieve the maximum working capacity of the adsorbent.

Multiple adsorbent beds operating in parallel may also be required for heat transfer reasons. Unlike liquid phase adsorption, gas phase adsorption is sensitive to temperature. Because of the poor heat transfer in fixed adsorbent beds, particularly carbon beds, multiple small-diameter adsorbent beds may be necessary to provide adequate rates of heat transfer to the center of the bed during adsorption and desorption.

During adsorption, temperatures above the ignition temperature of the organic can occur within the bed (particularly where the organic loading rate of the adsorbent is high) unless adequate heat transfer is possible. Good heat transfer is also important in the desorption cycle because desorption results in bed cooling. This cooling is undesirable because the rate of desorption decreases as temperature decreases. For this reason, the desorption process is usually carried out at temperatures above the adsorption temperature to increase desorption kinetics and adsorbent working capacity. Since complete desorption is generally not economically feasible, a residual amount of the adsorbant remains on the adsorbent after desorption. The adsorbent's working capacity is the difference between the amount adsorbed and this residual amount.

Adsorbent bed regeneration (desorption) is accomplished by applying a vacuum or low-flow purge with hot air or steam. The effluent from desorption may then be sent to a low-temperature condenser to recover the organics or incinerated. In either option, the adsorption operation functions as a concentration step to improve the performance and reduce the cost of condensation or incineration operations.

5.3.4.1.2 Process operation--

Applicable Feed Streams--The following guidelines should be considered when selecting waste streams for air stripping/adsorption pretreatment:

- The organic solutes should have high Henry's law constants (for the actual waste stream) greater than approximately 10^{-4} atm;
- The waste stream should be basically suitable for liquid phase adsorption treatment except that air stripping can accommodate (1) high concentrations of suspended solids, or (2) high levels of high molecular weight organics relative to the level of the more volatile low molecular weight organics.

Process Emissions and Wastes--The output streams include: (1) the treated waste effluent from the stripping column, (2) the adsorber effluent air, (3) the recovered condensate, and (4) the desorption purge air from the condensing unit. With the proper design and operation of the adsorber and condensation units, there should not be any environmental impact from the output streams 2, 3, and 4.

Removal Efficiency--Air stripping generally removes organics from the liquid waste stream with better than 99 percent efficiency, and the efficiency increases as the Henry's law constant increases. The recovery efficiency of the adsorption system is typically above 99.9 percent.

5.3.4.1.3 Existing sites--No specific sites using air stripping/adsorption treatment have been identified. However, both the air stripping and vapor phase adsorption process are mature technologies and are widely used in the chemical process industries. The major application of air stripping in waste treatment is for the removal of ammonia from wastewater.

5.3.4.1.4 Process economics--The major process variables that affect the economics of this treatment method are: Henry's law constant of the solute for the particular waste stream, the waste stream flow rate, and the adsorbent's capacity for the organic solute(s).

The size of the air stripping column is governed primarily by Henry's law constant and the required removal (stripping) efficiency. A high Henry's law constant reduces the mass rate of air required per unit mass of waste flow. Column height increases as the required removal efficiency increases.

The size of the adsorber increases as the total amount of organics stripped increase and as the concentration of the organics in the stripper effluent decreases. Like liquid phase adsorption, the efficiency of adsorbent utilization increases as the adsorbate concentration in the adsorber influent increases.

Another important economic factor in the adsorption step is the pressure drop across the adsorber. There is a trade-off between the cost of a blower that will be capable of handling high pressure drops and the mesh size of the carbon required. Large mesh adsorbents, which are considerably more expensive (especially activated carbon), will be required if low pressure drop-adsorbers are used.

5.3.4.2 Example Case: Air Stripping/Adsorption--

5.3.4.2.1 WET stream--The example system for air stripping/carbon adsorption, is designed to process 500 kg/h of caustic scrubber effluent from perchloroethylene and carbon tetrachloride production. This waste stream influent to the treatment system corresponds to stream 02.02.20 of the WET Model Data Base.

5.3.4.2.2 Process flowsheet--Estimated capital and operating costs have been developed for a combined treatement system that includes continuous packed-bed air stripping and GAC adsorption. This system is shown in Figure 5-9. The GAC system component is a fixed-bed unit with air-purge adsorbent regeneration and condensation recovery of the organic adsorbate.

The packed-column stripper is designed to process 500 kg/h of liquid influent with 99.9% removal (transfer to the air stream) of the carbon tetrachloride from the liquid stream at a concentration of 0.013 kg CCl_4/kg solution. The GAC fixed-bed adsorbers, which operate in cyclic fashion between an adsorption and a desorption mode, are designed to capture better than 99.9% of the carbon tetrachloride in the air stream effluent from the packed-bed stripper. The GAC columns are desorbed (reactivated) by a small volume air purge/vacuum technique. The organics desorbed from the GAC are condensed and recovered.

Operating for 365 days per year (@ 24 h/day), the air stripping/ GAC adsorption system would treat 4,380,000 kg/yr waste and remove or recover approximately and 56,940 kg CCl_4/yr.

5.3.4.2.3 Economics--The total capital cost (line items are shown in Table 5-13) is estimated to be $263,000 (January 1983 dollars). Discounting the capital costs at 10 percent over 10 years results in a total annualized cost of $92,180/yr. The unit cost is estimated to be $0.0182/kg waste treated.

5.3.4.3 Advantages and Disadvantages--

The major advantages of air stripping/adsorption pretreatment for hazardous waste streams are:

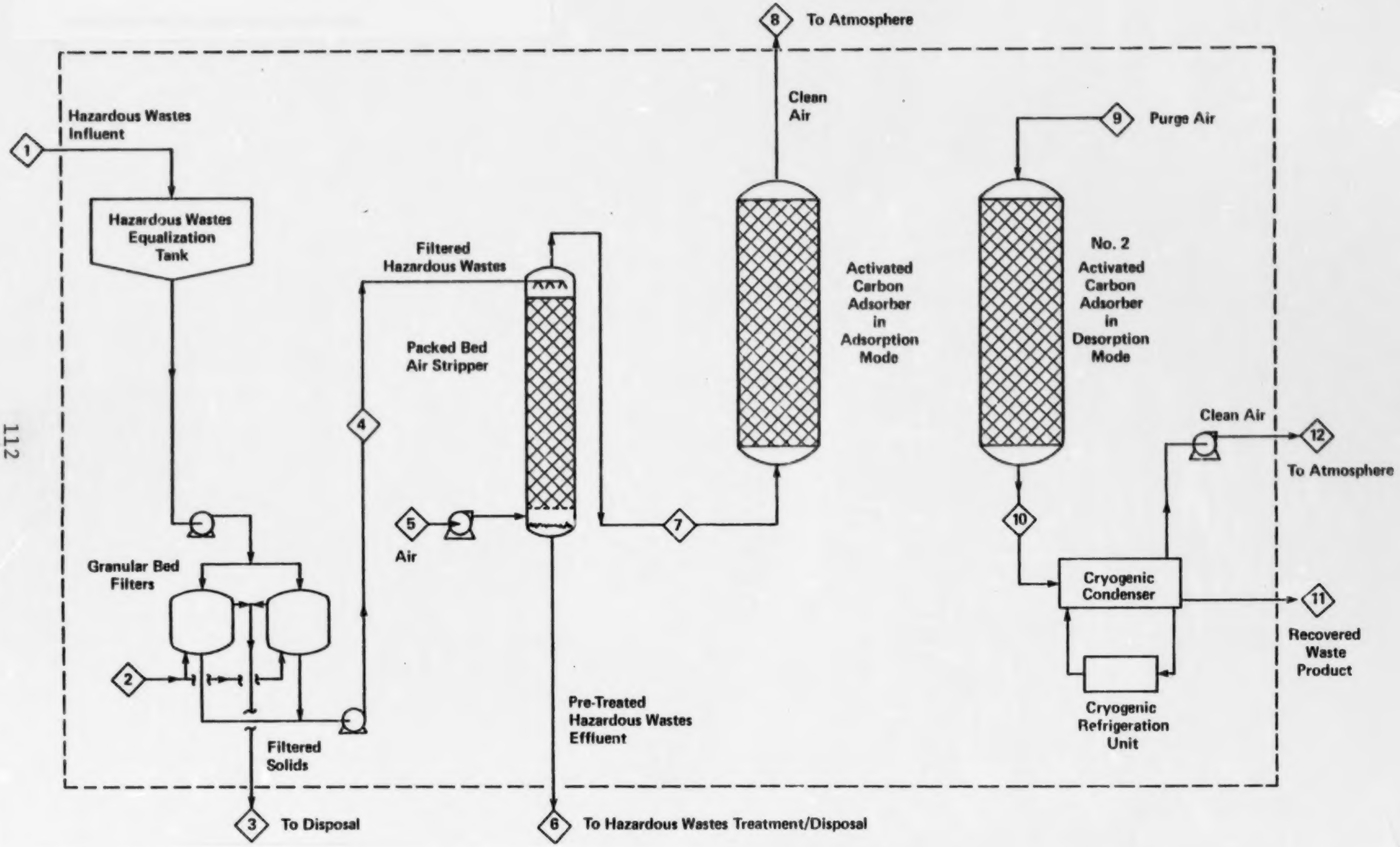

To Atmosphere
8
Clean Air
Hazardous Wastes Influent
1
Hazardous Wastes Equalization Tank
9
Purge Air
No. 2 Activated Carbon Adsorber in Desorption Mode
Activated Carbon Adsorber in Adsorption Mode
Filtered Hazardous Wastes
Packed Bed Air Stripper
4
Clean Air
12
To Atmosphere
5
Air
7
10
Granular Bed Filters
Cryogenic Condenser
11
Recovered Waste Product
2
Pre-Treated Hazardous Wastes Effluent
Cryogenic Refrigeration Unit
Filtered Solids
3
To Disposal
6
To Hazardous Wastes Treatment/Disposal

Figure 5-9. Process flow sheet for air stripping/carbon adsorption pretreatment to remove volatile constituents from hazardous waste.

	Stream Components (kg/h)					
Stream Number	Carbon Tetrachloride	Solids	Nonwater	Water	Air (dry)	Total
1	6.5	2.5	47.0	444.0	–	500.0
2	–	–	–	5.2	–	5.2
3	–	1.5	–	4.2	–	6.7
4	6.5	1.0	47.0	444.0	–	498.5
5	–	–	–	3.8	478.2	482.0
6	–	1.0	47.0	–	444.0	492.0
7	6.5	–	–	4.8	478.2	489.5
8	–	–	–	4.8	478.2	483.0
9	–	–	–	0.08	9.02	10.0
10	6.5	–	–	0.08	9.02	16.5
11	6.5	–	–	0.08	–	6.58
12	–	–	–	–	9.02	9.02

Figure 5-9 (continued).

TABLE 5-13. CAPITAL AND OPERATING COSTS FOR AIR STRIPPING/ADSORPTION TREATMENT SYSTEM FOR WASTE STREAM 02.02.20

Capital Costs	
Packed column air stripper system	$145,000
Carbon adsorption columns (4 required)	16,000
Condenser/refrigeration system (10 ton unit @ $1,500/ton)	15,000
Carbon inventory (5,300 lb @ $2.00/lb)	10,600
Construction cost[a]	76,500
Total Capital Costs	$263,100
Annualized Operating Costs	
Operating labor (1,000 man-hours @ 15/m-h)	$15,000
Maintenance (5% of capital cost)	13,200
Electricity (163,000 kWh @ $0.05/kWh)	8,150
Steam (600,000 lb × $4.00/1,000 lb)	2,400
Taxes, insurance, administration (4% of capital cost)	10,530
Capital recovery (16.3%; 10% over 10 years)	42,900
Total Operating Costs	$92,180
Product Recovery Credit (125,260 lb @ $0.10/lb)	12,530
Net Operating Costs	$79,650
Waste treated (kg/yr)	4,380,000
Total volatiles removed (kg/yr)	56,940
Unit treatment cost ($/kg waste treated)	0.018 $/kg
($/kg volatiles removed)	1.40 $/kg

[a] Construction fee (10%), contingency (15%), engineering (15%), startup (1%).

- The process operations are mature technologies that can be designed for particular applications with a high degree of reliability.
- The process is simple and requires minimal labor for operation and maintenance.
- Valuable organic materials may be readily recovered.
- Adsorbent regeneration is carried out in situ without the routine need for inventory replacement.

The major disadvantage of air stripping/adsorption pretreatment is:

- Air stripping is limited to those streams where Henry's law constants of the solute are favorable. In the case of waste streams with multiple solutes requiring removal, only some of the solutes are likely to have favorable liquid-vapor partitioning characteristics.

5.3.4.4 Recommendations--

The following recommendations are offered:

1. Henry's law constants should be determined for the actual waste streams that are judged to be suitable preliminary candidates for air stripping/adsorption pretreatment.
2. A pilot-scale stripping/adsorption unit should be developed and field evaluation tests conducted.

5.3.5 Evaporation/Adsorption

This waste treatment method parallels closely the air stripping/adsorption treatment process described previously in Section 5.3.4. Like the air stripping/adsorption process, this method is design to treated waste streams where the physical nature of the stream does not allow direct contact with a carbon or resin adsorbent. For example, evaporation/adsorption may be a viable alternative for waste streams that are suitable for adsorption treatment but contain high levels of suspended solids.

5.3.5.1 State of the Art--

5.3.5.1.1 Process description--Evaporation/adsorption, like air stripping/adsorption, involves three major process operations: (1) evaporation of the solute from the waste stream (physical separation), (2) adsorption (vapor-solid contacting), and (3) adsorbent regeneration/adsorbate recovery.

The main objective of heating the waste stream is to increase the vapor pressure of the organic solutes. This may be accomplished in the conventional multieffect evaporators or in solids drying equipment with internal material mixing if the waste stream is a sludge or is highly viscous. By heating the waste stream, the dissolved organics will evaporate and in addition suspended organics may also evaporate.

In this treatment process the waste stream is sent to an evaporator where the stream is heated to a controlled temperature and the generated vapor is removed from the evaporator either by air purge or vacuum. This vapor effluent is then passed through an adsorbent bed where the organic species are adsorbed. In the case of some aqueous streams where a high percentage of the vapor is water, condensation of part of the water vapor in the evaporator effluent may be beneficial to reduce the volume of vapor going to the adsorber(s).

The adsorption system consists of multiple fixed-bed adsorbent columns (contactors); part of the columns are on-stream adsorbing organics from the evaporator effluent while the remaining ones are off-stream being regenerated.

Adsorbent regeneration is accomplished by either vacuum desorption or low-flow purge of the bed with heated air or steam. The effluent from the adsorbent bed during regeneration is sent to a low-temperature condensation system where the organic vapors are recovered. Direct condensation of the volatile-containing gas, an alternative to carbon adsorption, is very energy intensive unless the volatile is highly concentrated since the entire gas stream must be cooled. In this sense, carbon adsorption can be considered as a concentrator of the volatile.

5.3.5.1.2 Process operation--

Applicable Feed Streams--This treatment method is an alternative to the carbon and resin adsorption methods in cases where the suspended solids level of the waste stream is too high for prefiltration and direct liquid phase adsorption. It is particularly suitable for the treatment of sludges and viscous waste streams.

This process would also be a candidate for the treatment of nonaqueous waste streams containing highly volatile low molecular weight organics and comparable or higher concentrations of significantly less volatile high molecular weight organics. The direct liquid phase adsorption of this type of multicomponent waste stream would result in early adsorbent-bed breakthrough of the lower molecular weight components. By evaporative (physical separation) treatment of such waste streams, the high vapor pressure constituents would be concentrated in the vapor phase where they could then be more efficiently adsorbed.

Process Emissions and Wastes--The output streams of the combined evaporation/adsorption treatment process are essentially the same as those for the air stripping/adsorption process described in Section 5.3.4.1.1

Removal Efficiency--The removal efficiency depends mainly on the difference in vapor pressure between the organic solute and the particular solvent (if the operating intent is not to achieve complete evaporation). At complete evaporation of the entire liquid phase, the removal of the volatile organics from the waste stream is 100 percent. The capture of the evaporated organics in the adsorption system is typically above 99.9 percent.

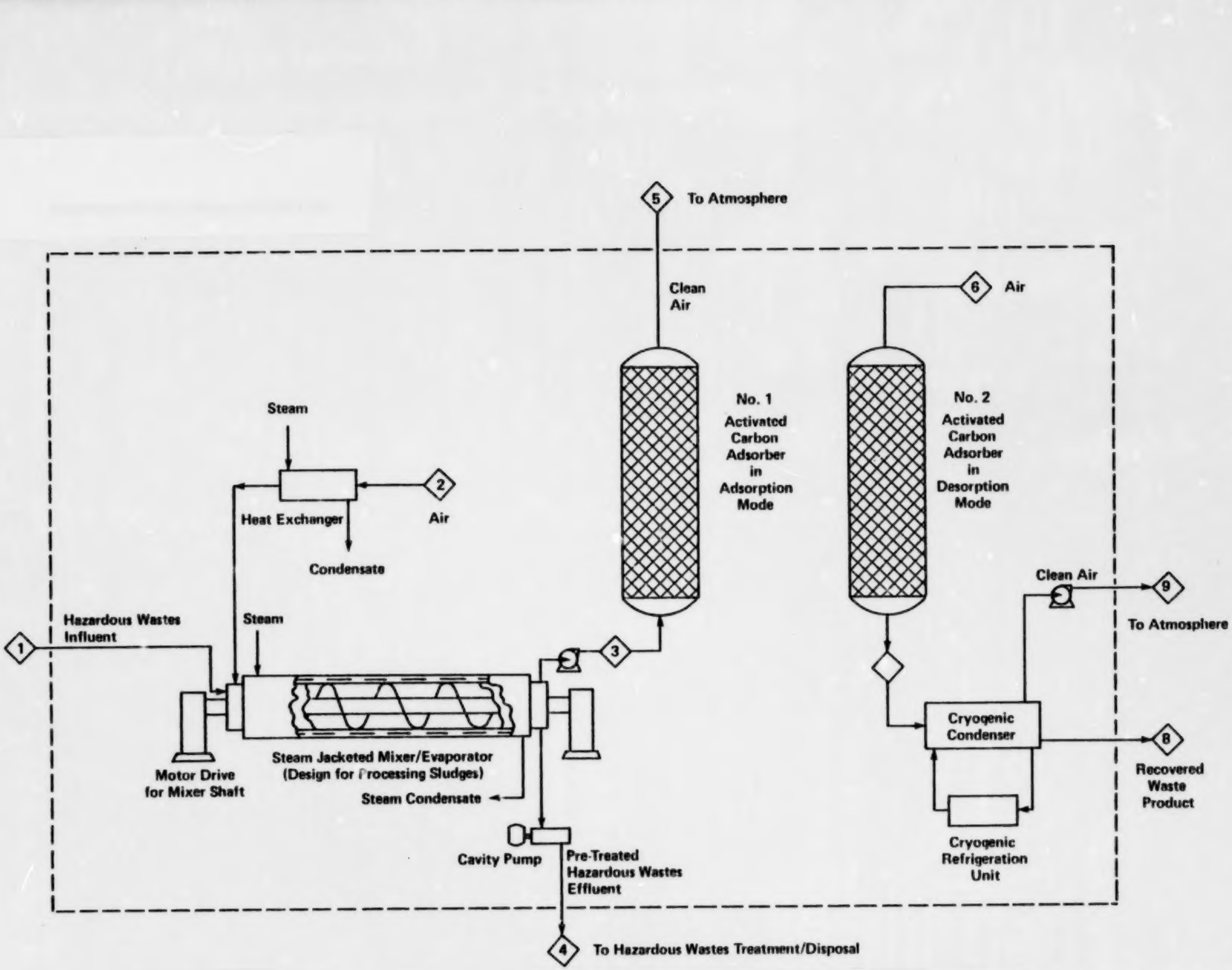
State of Recovered Volatiles--The volatiles are recovered in the condensation system in a liquid state.

5.3.5.1.3 Existing sites--No waste treatment facilities that use the combined evaporation/ adsorption system were identified. Nevertheless, all the operational steps of this combined system are mature technologies and are widely used in chemical process industries. Therefore, this treatment process can be reliably designed for a specific waste treatment application.

5.3.5.2 Example Case: Evaporation/Adsorption--

5.3.5.2.1 WET stream--The evaporation/adsorption system is designed to process 1,000 kg/h of distillation side cut from acetaldehyde production by ethylene oxidation. This waste stream influent to the treatment system corresponds to stream 03.04.14 of the WET Model Data Base.

5.3.5.2.2 Process flowsheet--Estimated capital and operating costs were developed for a combined treatment system including continuous evaporation and GAC adsorption. This system is shown in Figure 5-10. The GAC system component is a fixed-bed unit with air purge adsorbent bed regenera-



5
To Atmosphere
Clean Air
6
Air
Steam
No. 1 Activated Carbon Adsorber in Adsorption Mode
No. 2 Activated Carbon Adsorber in Desorption Mode
2
Heat Exchanger
Air
Condensate
Clean Air
9
To Atmosphere
Hazardous Wastes Influent
1
Steam
3
Cryogenic Condenser
8
Recovered Waste Product
Motor Drive for Mixer Shaft
Steam Jacketed Mixer/Evaporator (Design for Processing Sludges)
Steam Condensate
Cavity Pump
Pre-Treated Hazardous Wastes Effluent
Cryogenic Refrigeration Unit
4
To Hazardous Wastes Treatment/Disposal

Figure 5-10. Process flow sheet for evaporation/carbon adsorption pretreatment to remove volatile constituents from hazardous waste.

5-10

Stream Number	Stream Components (kg/day) Acetaldehyde	Acetyl Chloride	Chloral	Chloroacetaldehyde	Chloroform	Formaldehyde	Solids	Nonwater Residual	Water	Air	Total
1	3,888	2,616	1,752	2,856	480	480	480	168	11,200	–	24,000
2	–	–	–	–	–	–	–	–	–	4,000	4,000
3	3,888	2,616	1,752	2,856	480	480	–	–	350	–	16,422
4	–	–	–	–	–	–	480	168	10,850	–	11,498
5	–	–	–	–	–	–	–	–	350	4,000	4,350
6	–	–	–	–	–	–	–	–	–	121	121
7	3,888	2,616	1,752	2,856	480	480	–	–	–	121	12,193
8	3,888	2,616	1,752	2,856	480	480	–	–	–	–	12,072
9	–	–	–	–	–	–	–	–	–	121	121

Figure 5-10 (continued).

tion and condensation recovery of the organic adsorbates. The evaporator, which is a screw conveying-type of steam-jacketed heat exchange, is designed to process 1,000 kg/h of liquid/ slurry wastes with essentially 100 percent vaporization of the organic constituents. For the example case, the waste stream influent to the evaporator has the composition shown below.

	Mass fraction
Acetaldehyde	0.162
Chloroacetaldehyde	0.119
Chloroform	0.020
Formaldehyde	0.020
Solids	0.020
Water/other nonwater	0.659

The evaporator is purged with heated air that is then passed through the GAC fixed-bed column where the organics are removed from the air stream. The GAC columns are periodically regenerated by desorbing the organics by an air purge/vacuum technique. The adsorbates desorbed from the GAC are then condensed from the purge stream and recovered.

Operating for 365 days per year (@ 24 h/day), the evaporation/GAC adsorption system would treat approximately 8,760,000 kg waste/yr and recover approximately 4,355,000 kg/yr of organics.

5.3.5.2.3 Economics--The estimated capital and operating costs for treatment of the waste stream 03.04.14 are shown in Table 5-14. The total capital cost is estimated to be about $2,317,000 (January 1983 dollars). Discounting the capital costs at 10 percent over 10 years results in a total annualized cost of $822,000/yr. If the recovered organics are sold, an estimated credit of $218,000/yr may be applied against annual operating costs to give a unit treatment cost of $0.0689/kg waste treated.

5.4 BIOLOGICAL TREATMENT

5.4.1 Introduction

Biological treatment is the most common method of removing organic compounds from aqueous streams. In addition, it has been employed to

TABLE 5-14. CAPITAL AND OPERATING COSTS FOR EVAPORATION/GAC ADSORPTION TREATMENT OF WASTE STREAM 03.04.14

Capital Costs	
Evaporator system	830,000
Carbon adsorption columns (6 required)	48,000
Condenser/refrigeration system (30 ton unit @ $1,500/ton)	45,000
Carbon inventory (360,000 lb @ $2.00/lb	720,000
Construction cost[a]	674,000
Total installed costs	$2,317,000
Annualized Operating Costs	
Operating labor (4,400 man-hours @ 15/m-h)	66,000
Maintenance (5% of capital cost)	116,000
Electricity (400,000 kWh @ $0.05/kWh)	20,000
Steam (37.2×10^6 lb @ $4/1,000 lb)	149,000
Taxes, insurance, administration (4% of capital cost)	93,000
Capital recovery (16.3%; 10% over 10 years)	378,000
Total Operating Costs	$822,000
Product Recovery Credit (4,355,000 kg @ $0.05/kg)	$218,000
Net Operating Costs	$604,000
Waste treated (kg/yr)	8,760,000
Total volatiles removed (kg/yr)	4,355,000
Unit treatment cost ($/kg waste treated)	0.069 $/kg
($/kg volatiles removed)	0.14 $/kg

[a] Construction fee (10%), contingency (15%), engineering (15%), startup (1%).

remove ammonia and nitrates. Removal of the contaminants occurs as they are used as food for microorganisms present in the stream. Organic materials are transformed partially into gases (CO_2, CH_4) and partially into additional cellular material for microorganisms. The vast majority of biological treatment systems for municipal and industrial waste employ aerobic organisms that use oxygen dissolved in the wastewater to oxidize organics to CO_2.

In aerobic systems, oxygen is transferred to the wastewater through air-water contact. This transfer is promoted to maintain enough dissolved oxygen in the wastewater so that the process is not limited by dissolved oxygen. Typically, this oxygen is supplied using surface aerators or submerged diffusers or by allowing the wastewater to flow over a surface in a thin film. All of these processes, as a consequence of promoting air-water contact, also promote stripping of volatiles to the atmosphere. As a result, they are unsuitable as pretreatment processes designed to decrease emissions of volatile chemicals to the atmosphere. Although closed aerobic systems have been designed and operated (e.g., UNOX, Union Carbide), they are rare and relatively capital intensive. Any attempt to recover volatiles from air effluents of aerobic systems would be better handled as air stripping processes.

Biological wastewater treatment processes operating without dissolved oxygen are termed anaerobic. These processes employ different species of organisms that convert dissolved organics to CO_2 and CH_4. The presence of oxygen in wastewater inhibits these organisms. Certain anaerobic wastewater treatment operations are, however, carried out in open lagoons. In these processes, the rate of biooxidation is high relative to the rate of reaeration from the surface, thus aerobic conditions prevail only in the upper layers of the lagoon, and anaerobic decomposition takes place simultaneously in the lower layers. Processes of this type are also unsuitable as pretreatments to decrease emissions of volatiles from wastewater; the relatively large surface areas exposed to the atmosphere and relatively long residence times (days, weeks, months) will result in emissions during pretreatment.

The remaining processes, i.e., anaerobic treatment in closed vessels, can be considered for use as pretreatments to decrease emissions of volatiles from hazardous wastes. The primary technical considerations are the biode-

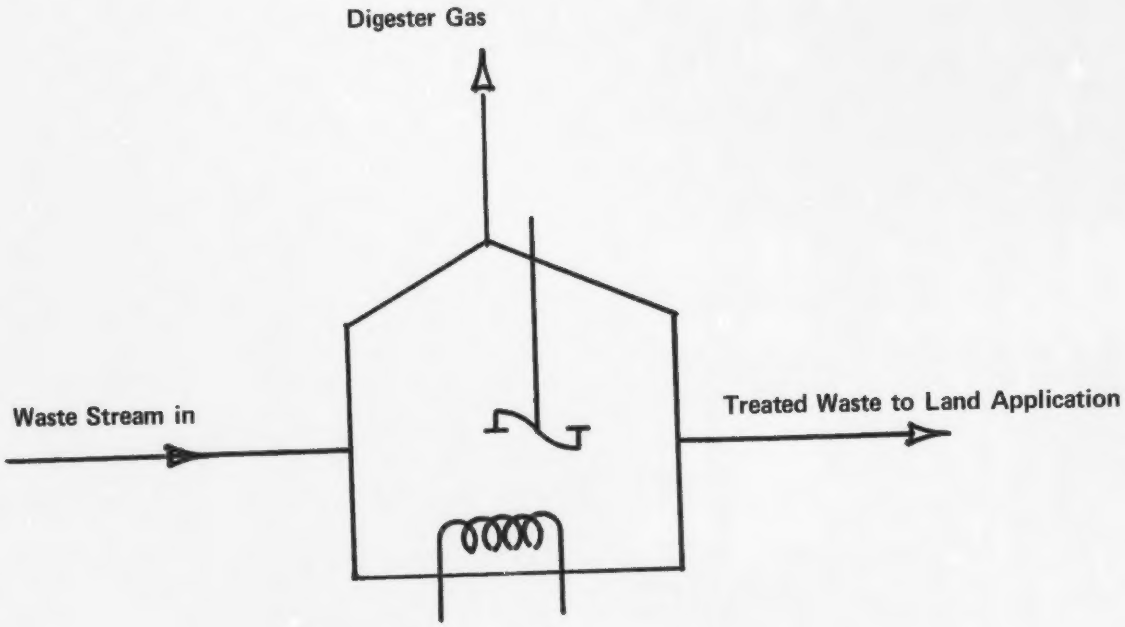

Digester Gas
Waste Stream in
Treated Waste to Land Application

Figure 5-11. General process diagram for anaerobic biological treatment.

5-11

gradability of the material to be removed and the potential toxic or inhibiting effects of other components in the waste stream.

5.4.2 State of the Art

5.4.2.1 General Process Description--

The basic process takes place in a closed vessel that is seeded with or allowed to develop an acclimated biological population. Wastewater is added and withdrawn either continuously, or more commonly, intermittently, and the product gases (chiefly CO_2 and CH_4) are withdrawn from the top of the vessel as they are produced and either collected or burned. The most frequent refinements to the process are heating and mixing. Anaerobic organisms (in contrast to aerobic wastewater treatment organisms) are thermophillic and most processes are operated at approximately 35° C. This heat can be supplied by circulating hot water through internal heating coils. The energy is usually provided by combustion of some or all of the methane produced in the vessel.

Other process variations involve recycle of biomass separated from effluent wastewater, staging of reactors, baffling, and immobilization of organisms on packing. A variety of proprietary reactor configurations are available, e.g. ANAMET, ANITRON, and CELROBIC, but relatively few installations of these processes are in operation.

5.4.2.2 Process Details--

A general process flow diagram is given in Figure 5-11. This diagram shows an anaerobic treatment process conducted in a stirred heated vessel. More elaborate processing schemes might involve baffled vessels (to approach plug flow), sequential mixed vessels, or biomass separation from the effluent with recycle to the process vessel.

The most common use of anaerobic biological treatment in closed vessels is for digestion of sludge produced in aerobic treatment of municipal wastewater. At present, commercial use of anaerobic biological treatment has been limited almost entirely to agricultural and food processing wastes. Application of this technology has been reported for winery wastewater (Stander 1966), packing house waste (Schroepfer et al. 1955), wheat starch wastewater (Taylor 1972), beet sugar and potato wastewater (Pette and Verspille 1982), vegetable canning wastewater (Morfaux et al. 1982), brewery waste (Keenan and Kormi 1981), and palm oil sludge (Chin 1981).

Recent research in the anaerobic treatment of organic chemicals in wastewater has indicated that a wide variety of materials are biodegradable although rates may not be rapid enough to make the technology practical. Speece (1983) has compiled a list of approximately 60 organic compounds amenable to anaerobic treatment. Lettinga et al. (1981) have reported on laboratory studies of anaerobic treatment of methanol and higher alcohols. Although the process was found to be feasible, the authors reported that biological activity was easily upset and very sensitive to trace elements. The treatment of more common agricultural and municipal wastes takes place in stages with organic acids such as acetic, butyric, and propionic formed as intermediates. For this reason, data are available for treatment kinetics of these materials (Lawrence and McCarty 1970).

5.4.2.3 Suitability--

Anaerobic treatment is suitable for aqueous organic solutions. The biodegradability of individual streams must be confined by laboratory and pilot plant testing. The presence of toxic metals in significant quantity will render the waste stream unsuitable. At present, halogenated organics are unsuitable for this technology. Organic acids, ketones, aldehydes, and esters are the most likely candidates. Streams of low volumes are most suitable due to the comparatively high residence times involved.

5.4.2.4 Associated Emissions--

The process produces two byproducts, gas and biomass. The gas must be controlled through either collection or flaring. If flared, ordinary combustion emissions must be controlled; i.e. unburned hydrocarbon and oxides of nitrogen. If sulfur-containing compounds are present in the waste stream, reduced sulfur gases will be present in the gas and, upon flaring, oxides of sulfur will be produced and require control.

If the gas is burned onsite either in a boiler or in an internal combustion engine, the same considerations apply to the exhaust gases as to the exhaust gas from flaring. The gas can be upgraded to pipeline quality methane by removing CO_2, H_2S, and moisture. This can be accomplished with conventional natural gas processing technology.

The biomass produced in the process will, in a completely mixed system, be present in the treated effluent. In some reactor configurations, this effluent is separated from the pretreated wastewater and a portion recycled to the reactor. Ultimately, some biomass is wasted from the process as a sludge regardless of configuration. If the ultimate disposal method of the pretreated wastewater is land application, no separation is required and the sludge can be applied with the pretreated wastewater. If additional processing of the pretreated wastewater is required, the sludge can be separated by sedimentation; dewatered by filtration, centrifugation, or thermal drying; and incinerated or landfilled.

The pretreated waste stream must still be disposed of either by land application, further treatment, or discharge to a treatment works. Higher levels of treatment could be achieved in multistage equipment, at additional cost, that might permit reuse of wastewater. In the event of reuse or discharge, biomass present in the pretreated wastewater would be removed by sedimentation. This material would be incinerated after drying. The removed volatile is destroyed in the process. A concentrated residue stream is not produced.

5.4.2.5 Existing Sites--

A list of current application is given in Table 5-15. At present, this technology is not commonly used for the treatment of hazardous wastes in the United States.

5.4.2.6 General Economics--

Keenan and Kormi (1981) estimated that anaerobic treatment of a 7,300-ft^3/day stream of brewery waste would produce methane at a cost of \$1.19/1,000 ft^3 considering annualized capital cost of the plant and all operating costs. The U.S. EPA (1974) estimates total treatment cost for anaerobic digestion of sewage sludge at \$0.60 to \$1.50 (1972) per 1000 ft^3, based on retention times of 10 to 15 days.

5.4.3 Example Case

5.4.3.1 WET Stream Chosen--

WET Stream 02.02.12, "Heavy ends from ethylene oxide production from ethylene," has been chosen for removal of acetaldehyde by anaerobic biological treatment. This is an aqueous stream containing 15.8 percent acetaldehyde produced at 2800 kg/day.

TABLE 5-15. EXISTING ANAEROBIC TREATMENT SITES

- Municipal wastewater treatment
  - Primary sludge
  - Waste activated (aerobic) sludge
- Small-scale domestic wastewater treatment
  - Septic tanks
- Agricultural/food processing wastes
  - Winery
  - Packinghouse
  - Feedlot
  - Brewery
  - Starch
  - Sugar
  - Palm oil
  - Cannery

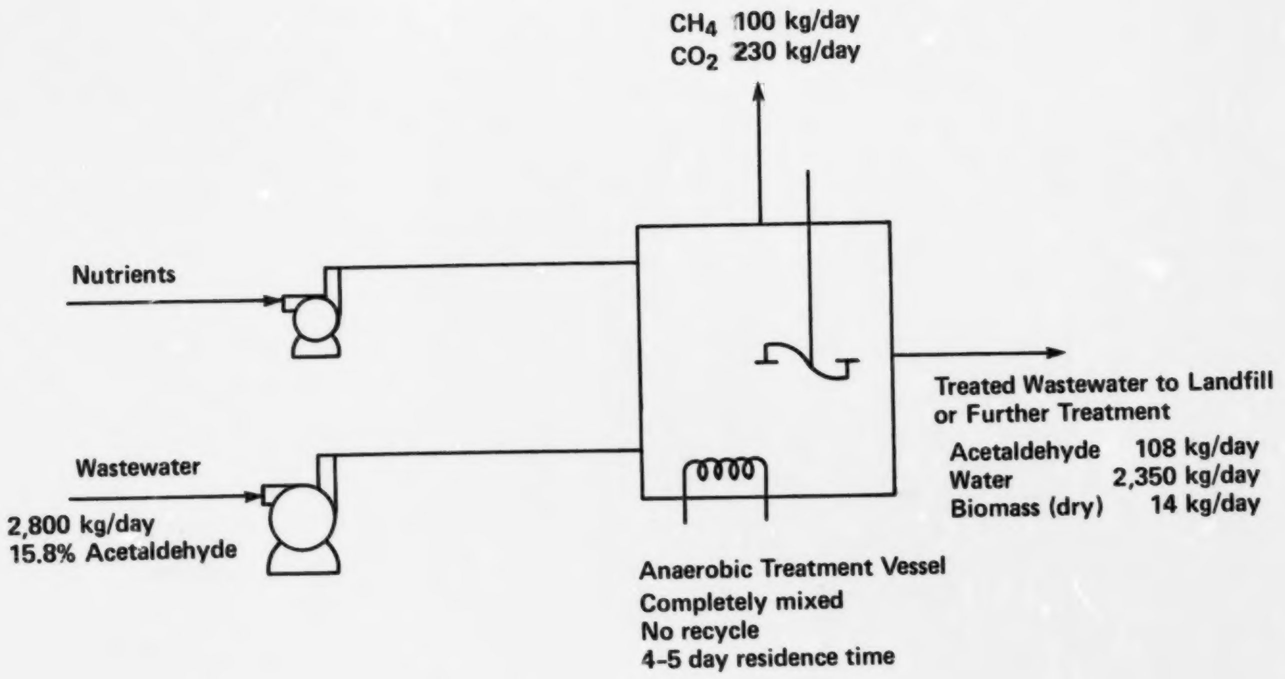

CH_4 100 kg/day
CO_2 230 kg/day
Nutrients
Wastewater
2,800 kg/day
15.8% Acetaldehyde
Treated Wastewater to Landfill
or Further Treatment
Acetaldehyde 108 kg/day
Water 2,350 kg/day
Biomass (dry) 14 kg/day
Anaerobic Treatment Vessel
Completely mixed
No recycle
4-5 day residence time

Figure 5-12. Process flow sheet for anaerobic biological treatment of WET stream 02.02.12.

TABLE 5-16. TREATMENT OF WET STREAM 02.02.12 HEAVY ENDS FROM ETHYLENE OXIDE PRODUCTION FROM ETHYLENE

	kg/day
IN:	
Wastewater	
Acetaldehyde	440
Water	2,360
Nutrients	
Ammonia	20
Phosphoric acid	1
	2,800
OUT:	
Treated wastewater	
Acetaldehyde	110
Water	2,360
Biomass (dry)	14
Gas	
CO_2	230
CH_4	100
	2,800

5.4.3.2 Process Details--

A simplified flow sheet for anaerobic biological treatment of WET stream 02.02.12, "Heavy ends from ethylene oxide production from ethylene," is given in Figure 5-12. A mass balance for this process is given in Table 5-16. The process as shown removes about 75 percent of the acetaldehyde from the wastewater with a residence time of 4 to 5 days. Biological rate constants have been estimated to be roughly those determined for acetic acid. Higher levels of treatment could be obtained by separating biomass from effluent wastewater and returning it to the treatment unit.

The uncertainties affecting the choice of this technology center on the reaction kinetics; i.e. how large a vessel must be provided. In addition, the presence of other components in the waste stream besides acetaldehyde that may have a toxic or inhibitory effect must be determined. Finally, the sensitivity of the system to fluctuations in flow and concentration during expected periods of shutdown for maintenance, strikes, inventory reduction, etc., must be determined.

The key design variables are extent of treatment (i.e., residence time) and reactor configuration. Depending on reaction rate, a more complex reactor incorporating recycle or multistage processing may be desirable.

5.4.3.3 Economics (Cost-Effectiveness)--

For large systems, U.S. EPA (1972) cost data for municipal sludge digestion can be used to estimate treatment costs. For much smaller capacities such as WET stream 02.02.12, a reasonable estimate of installed capital costs is $50,000, based on the cost of stirred heated tankage. The capital cost for such a system over 20 years at 12 percent would be approximately $0.024/gal. Depending on climate conditions, operating costs could be partially or completely offset by byproduct credit for methane generated. An additional cost of $0.02 to $0.09/gal for land application of the treated waste must be added.

5.4.4 Advantages and Disadvantages

The advantage of anaerobic treatment (and biological treatment in general) is that it is a low cost, low technology operation using simple equipment. Temperature and pressures are only slightly above ambient for anaerobic treatment (e.g., 35° C, 1 psig). Under some circumstances, the process can produce a net energy product after heating and mixing requirements are satisfied. One option is to drive the mixer with an internal combustion engine powered by the product gas from the process. Engine coolant can be circulated through coils in the vessel to maintain the temperature.

There are several important disadvantages to this technology. Perhaps the most important is that the process is not well developed for hazardous waste applications, and even for agricultural waste, operating experience is limited. Biological systems and anaerobic systems in particular are more sensitive to process upsets than chemical systems. The consequences of process upsets are greater than those in a chemical or physical system as the reestablishment of an acclimated culture following an upset may take weeks. A rapid change in waste stream composition, such as the introduction of a toxic trace metal, may wipe out the waste treatment capability.

Operation on a seasonal or intermittent basis may require reacclimation, with a consequent period of low waste treatment capacity each season. Similarly, an interruption in the process that produces the wastewater will disrupt the treatment system.

Sulfate-sulfur or organic sulfur compounds present on waste streams will generally be converted to hydrogen sulfide and other reduced sulfur compounds. These are volatile and toxic and have unpleasant odors even at low concentrations. Combustion of product gas from anaerobic treatment of wastes containing sulfur compounds will result in formation of sulfur oxides that may require control.

5.4.5 Recommendations for Further Study

Each individual waste stream would have to be tested for suitability in laboratory studies. The presence of certain chemicals toxic to the organisms responsible for treatment can make an individual waste stream unsuitable even if the components of interest have been found to be removable in other studies. In addition, the presence of other materials in the waste stream may affect the kinetics of removal; biological rate constants must be determined to permit accurate sizing of equipment.

Finally, nutrients such as nitrogen and phosphorus must be added if the waste stream contains insufficient levels of these elements. Optimal nutrient addition levels can be determined in laboratory studies.

5.5 OZONATION/RADIOLYSIS

5.5.1 Introduction

Ozonation/radiolysis is the process of oxidizing organic materials by reaction with ozone in the liquid or vapor phase. Ozone can be generated by an ozone generator or by radiation. Radiation can be used in conjunction with ozonation to generate additional ozone in-situ, make the organic molecules more reactive, and cause the ozone to form even more reactive species. The ultimate products from the destruction of hydrocarbons are carbon dioxide and water.

Ozonation/radiation can be used to remove volatile materials from hazardous waste. In a typical process, ozone would be produced by an ozone generator and brought into contact with the hazardous waste. A radiation source would be present to irradiate the vapor space of the gas-liquid contactor. In one version of this process, water and any condensates would be removed from the offgas and much of the gas would be recycled to an oxygen plant. The oxygen plant would then produce an oxygen rich gas which would feed the ozone generator.

5.5.1.1 Ozonation--

Over 40 years ago, it was demonstrated that some carcinogens are transformed by air containing ozone to less carcinogenic or noncarcinogenic materials (Tipson 1965). Out of concern for the carcinogenic potential of hydrocarbon effluents in water pollution from the thermal processing of mineral fuels, Il'nitskii et al. (1968) and Moriconi and Salce (1968) investigated the effect of ozone on several polynuclear aromatic compounds (PNAs). They concluded that ozonation was a potent technique for the deactivation of PNAs.

Ozone is produced from the three-body reaction:

$$O\cdot + O_2 + M \rightarrow O_3 + M$$

where M is a third body serving as an energy transfer medium. Elemental oxygen, $O\cdot$, is formed by the radiation-induced decomposition of oxygen, nitrogen dioxide, or carbon dioxide. The energy required to form molecular oxygen can be provided by heat, electromagnetic radiation, corona discharge, or fast electrons. Ultraviolet light is the primary mechanism for the production of terrestrial ozone and is also employed for small-scale ozone production. Ozone produced by UV is usually generated in air and delivered in concentrations of several ppm maximum.

5.5.1.2 Radiolysis--

Radiolysis involves the interaction of electromagnetic rays, or photons, with hazardous waste. The use of relatively low energy photons is often referred to as photolysis. The destruction and modification of waste material by photons in sunlight is an example of naturally occur radiolysis. Low energy photons may be generated by mercury arc lamps and ultraviolet (UV) fluorescent lamps. High energy photons (X-rays and gamma rays) can be generated by electron accelerators, radioisotope decay, and nuclear reactors.

The radiolysis of waste materials is a complex process, and many different types of chemical events can occur. In the presence of oxygen, even low energy photons can create ozone and singlet oxygen, both of which are powerful oxidizing agents. Thus, the use of radiolysis for the destruction of hazardous materials should not be isolated from the effect of ozonation. In fact, in many chemical systems, a synergistic effect is probable; the combined effect of radiolysis and ozonation can be greater than the contribution of the separate processes.

The use of radiolysis to destroy volatile organic compounds involves the interaction of radiation with matter. Electromagnetic radiation is attenuated as it passes through matter. This reduction in radiation is due to energy absorption and scattering by a fraction of the irradiated molecules. Absorbed electromagnetic radiation is rapidly converted into fast moving electrons which are indirectly responsible for the chemical changes that take place. The reaction of organic molecules in the gas phase is generally rapid, whereas liquid and solid phase reactions are generally slower. Therefore, ozonation/radiolysis for the removal of volatile compounds is expected to be more effective in the vapor phase than in the liquid phase.

High energy radiation, photolysis, and ozonation can be responsible for similar effects in reacting organic constituents of hazardous waste. Neish (1950) reported identification of 1,6- and 3,6-benzo(a)pyrenequionones from benzo(a)pyrene (BaP) irradiated with visible light in the presence of iodine. The same products were also identified in the degradation products of BaP from Cobalt-60 (gamma rays) by Milazzo et al. (1960). The products of UV-induced decomposition of BaP dissolved in benzene were identified by Masuda and Kuratsume (1966) as 6,12- and 1,6-benzo(a)pyrenequinone. Moriconi, Rahcozy, and O'Conner (1961) identified 1,6-, 3,6-, and 4,5-benzo(a)pyrenequinones by ozonation.

Although many hazardous materials are apparently protected from radiation-induced decomposition in the solid phase, radiation-induced decomposition can be more effective in solution. One postulated reason for the stability of concentrated solutions is that the first few layers of molecules attenuate most of the radiant energy (Kuratsume and Hirohata, 1961). However, dilute solutions of toxic organic molecules are quite susceptible to radiation decomposition. For example, the use of Cobalt-60 to decompose dilute BaP solutions is presented in Table 5-17 (Uibopuu et al. 1973). The BaP was protected in the benzene but was relatively rapidly decomposed in acetone. In octane, the effect was intermediate. Ethanol was the most effective solvent tested for decomposing the polycyclic molecule (Gubergritz et al. 1974).

5.5.1.3 Synergistic Effects of Radiation in Oxidizing Atmospheres--

Although either radiation or ozonation can independently degrade PNAs, the rates of decomposition under both ozonation and radiation are greater than a linear combination of the two effects, there is apparently a synergistic effect. At relatively low levels of ozone, the rate of decomposition of organics may not be appreciably different with or without irradiation. At higher levels of ozone, however, the synergistic effect may be much more pronounced. The synergistic effect of radiation and ozone is discussed in a literature review by Allen (1980).

In addition to reacting with ozone, organic compounds can also react with oxygen in a radiation field. Table 5-18 presents the results of an investigation of the effect of oxygen on the ultraviolet-induced decomposition of BaP in solution. The autocatalytic nature of the destruction of BaP suggests that ozone was being formed by the radiation.

TABLE 5-17. BaP DECOMPOSITION BY GAMMA RADIATION
(% Decomposition)

	Dose (Mrads)			
Solvent	0	1	2	4
Benzene	0	2.6	10.3	11.8
n-Octane	0	9.9	24.7	61.5
Acetone	0	44.2	74.5	95.5

TABLE 5-18. EFFECT OF OXYGEN ON THE ULTRAVIOLET-INDUCED DECOMPOSITION OF BaP IN SOLUTION (Kuratsume and Hirohata 1961)

	% BaP decomposition	
Time (hours)	Saturated N_2	Saturated O_2
24	8	22
48	16	64
114		100

Source: Kuratsume and Hirohata (1961).

5.5.1.4 Sources of Radiation--

Covalent bond energies of volatile organic molecules are typically of the order of 50 to 150 kcal/mole, and in order to cause bond breakage, electromagnetic radiation should be of greater energy. This requires visible light, ultraviolet light, accelerated electrons, X-rays, or gamma rays.

Solar radiation at the earth's surface is capable of initiating photochemical reactions. A number of studies have shown that sunlight can cause photodecomposition of pesticides and other contaminants in the environment. In most TSDF management operations (e.g., landfills), the waste stream generally would not have the retention time and exposed surface area required for effective treatment, particularly if exposure to sunlight is minimized as an indirect result of air emission controls. Ordinary fluorescent lamps can be used to simulate solar radiation; however, from this souce, radiation with enough energy has a relatively low intensity.

Low pressure mercury arcs (e.g., germicidal lamps) may be suitable for a treatment process if the volatile compound absorbs strongly at one of the lamp emission maxima. Medium pressure mercury arc lamps are of much greater utility for waste treatment than the low pressure mercury arc lamps. The high pressure mercury arc lamp is an order of magnitude more intense than the medium pressure lamp and has a broad, useful spectrum in the UV range.

High energy radiation sources include radioisotopes such as Cobalt 60. Higher energy radiation is more penetrating and suitable for waste treatment in large holding tanks, or process vessels.

The intensity of gamma rays provided by the decay of Cobalt-60 or other radioactive isotope gradually decays with time, typically of the order of years for most practical systems, requiring no energy input. sources of gamma radiation can be potentially obtained from waste nuclear material.

5.5.1.5 Ozonation Equipment--

Ozone reacts with itself and therefore must be generated either immediately prior to or during its application. It is also more efficient to produce in low concentrations. Most large-scale applications of ozone treatment are for biological purifications, such as destruction of bacteria and viruses. The technology for the application of ozone to aqueous streams is highly developed and can be readily adapted for industrial hazardous waste streams (Berkowitz et al. 1978).

For disinfection the ozone dose is typically used at concentrations less than 4 ppm in liquids. In industrial waste treatment applications, ozone is supplied at higher concentrations of 10 to 40 ppm in the waste. Typically the amount of ozone applied to the waste is 1.5 to 3 lb of ozone per lb of oxidizable organic. Ozone is generally produced at a concentration of about 1 percent by weight in air, up to a maximum of about 2 percent (or up to 6 percent maximum in oxygen) (De Renzo 1981). The ozone concentration used to treat the waste stream depends upon the mixing efficiency of the waste stream with the ozonized air and the design of the air/liquid contacting system.

Large-scale ozonators typically produce 10 to 500 lb of ozone per day at concentrations of 1 to 2 percent by weight (Murphy and Orr 1975). Construction materials that come in contact with ozone must be corrosion resistant (e.g., stainless steel, PVC, aluminum, teflon, and chromium plated metals).

5.5.2 State of the Art

Large-scale ozone treatment of aqueous waste material is a well-developed technology. Laboratory- and bench-scale studies have demonstrated that ozone can successfully treat hazardous waste components such as chlorinated hydrocarbons, dioxins, polynuclear aromatics, and pesticides. However, it has been used most often for the decomposition of large organic molecules in the laboratory. In addition, there are over 500 ozonation installations worldwide which use ozonation for the disinfection of water supplies. (De Renzo 1981).

Applications of ozonation to industrial waste treatment are not numerous, but feasibility has been demonstrated for cyanides and phenols (Berkowitz et al. 1978). Ultraviolet light is often used in conjunction with ozonation because of the synergistic effect discussed in Section 5.5.1.3.

Technology for large-scale application of photolysis for the removal of volatiles from hazardous wastes is not highly developed. Although pure photolysis is not likely to be a practical industrial waste treatment process within the next 5 to 10 years, photolysis processes may be used to enhance the destruction of hazardous materials by ozone.

Figure 5-13 presents a conceptual flow sheet for five different types of ozonation/radiolysis processes. These conceptual diagrams are presented to illustrate the variety of different processes that are possible using the principles of ozonation/radiolysis. In general, the radiation source would be UV from high intensity lamps, unless radiation of a bulk liquid or sludge is desired, in which case gamma radiation would be useful as in Processes A and B. The UV radiation is more efficient in the vapor phase than in the liquid and Process B shows an example of how air passing through the waste can be used to vaporize volatile organic material. These organic vapors are then destroyed in the vapor phase. In Process D, a waste liquid is pumped to the top of a reactor and sprayed across a radiation source. If the waste material was in a form which would tend to foul the surfaces of the UV lamps, higher energy radiation such as gamma rays would be more effective in Process D.

Sludges could not be processed with Process D, but Processes A, B, and C could conceptually process sludges.

When the waste in Process A is exposed to gamma radiation, it is important to have oxygen present to form ozone. In Process C, the ozone mixes with the waste in a more concentrated form, and the organic destruction would be much more rapid in Process C than in Process A. Process B would be preferred when there are volatiles mixed with relatively nonvolatile organics. Process B would selectively destroy the volatile organic compounds since the reaction occurs in the vapor phase. Process E involves using an oxygen plant to concentrate the oxygen feed for the ozone generator. The use of an oxygen plant could be practical in large systems because of the power savings from the ozone generator. With an oxygen plant, the gas is recycled, with some makeup air and some purging of oxidized products.

In summary, a wide variety of designs are possible for using ozonation/radiolysis processes. The choice of a particular design strategy would depend upon the waste composition, the form of the waste, the capacity of the process, and waste pretreatment requirements.

In general, ozonation/radiolysis can remove 95 to 99 percent of the volatile materials, depending on the process variables such as waste resi-

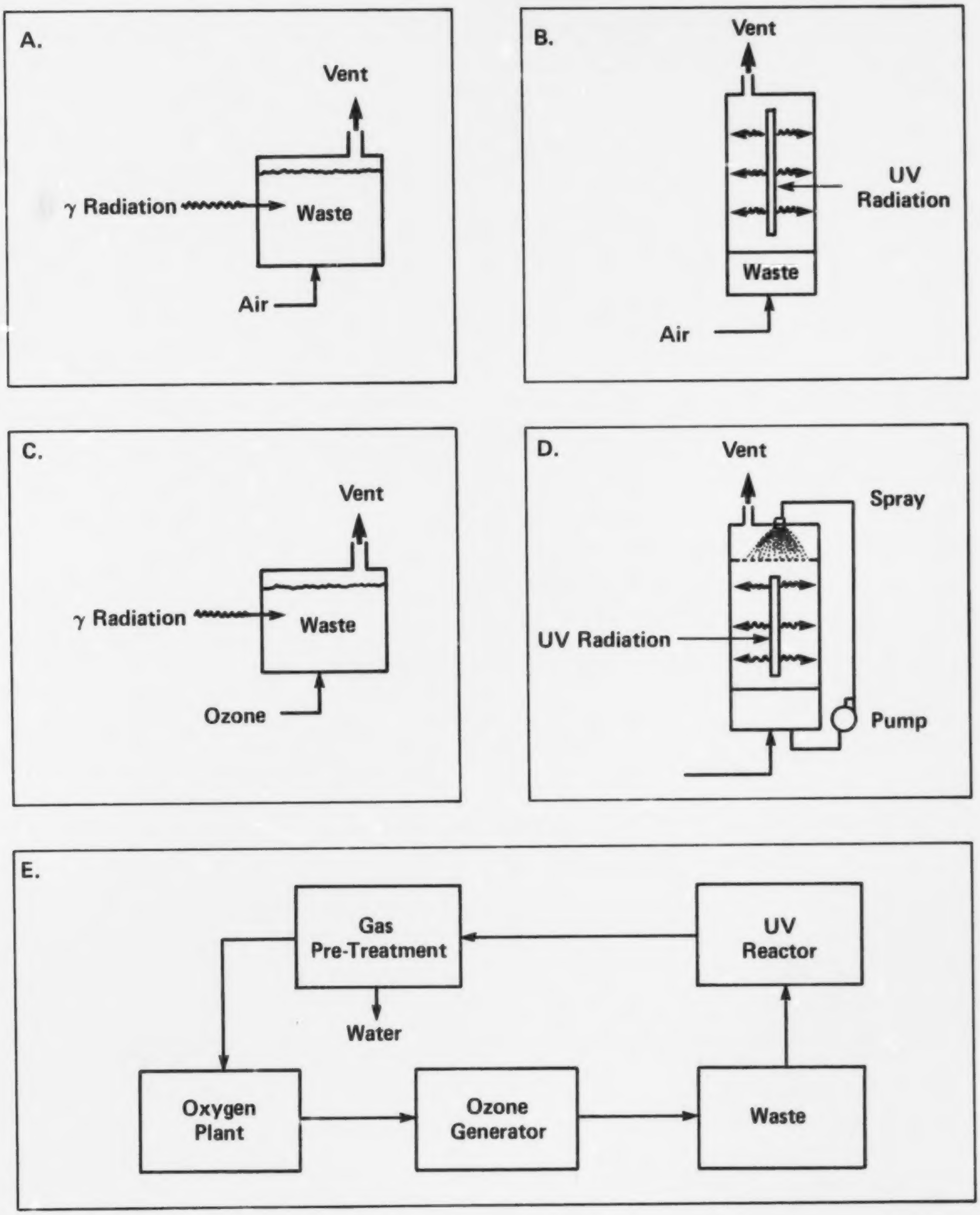

A.
Vent
γ Radiation
Waste
Air
B.
Vent
UV Radiation
Waste
Air
C.
Vent
γ Radiation
Waste
Ozone
D.
Vent
Spray
UV Radiation
Pump
E.
Gas Pre-Treatment
UV Reactor
Water
Oxygen Plant
Ozone Generator
Waste

Figure 5-13. Process flow sheet for five ozonation/radiolysis processes.

dence time, vapor residence time, reactor design, chemical characteristics of the wastes, and other factors.

5.5.2.1 Applicable Waste Streams--

The efficiency and residence time requirements for ozonation depend on both process equipment and the properties of the waste stream. Viscosity, agitation rates, contact equipment and other fluid and process variables are important. Another important factor is the opacity of the liquid to ultraviolet light. Since only surface reactions are probable for many liquid systems due to the shallow penetration of some forms of radiation, the rate of mixing is especially important for ozonation/radiolysis. Gamma rays are also capable of producing a synergistic reaction rate acceleration with ozone, but these are not attenuated at the surface of the liquid and tend to irradiate the entire bulk. High energy radiation is therefore useful for sludges and optically opaque liquids.

Generally waste streams containing greater than 5 percent organics would not be considered for ozonation/radiation pretreatment. Ozonation has been recommended for treating waste streams that contain less than 1 percent oxidizable hazardous components, as well as for preliminary treatment of more concentrated wastes for which there are no reasonable alternatives (Berkowitz et al. 1978). Potential exceptions include waste streams that separate into fractions more easily after UV/ozonolysis (e.g., wood preservative waste), waste streams that have extremely hazardous components (e.g., dioxins), and waste streams that have volatile components that are more susceptible to ozonation/radiolysis than most organic components. The waste stream requirements for suitability with ozonation/radiolysis is presented in Table 5-19.

In ozonolysis/radiolysis, it is important that the ozone be well mixed with the waste material and that the component to be treated is in the liquid or dissolved form. A cosolvent is sometimes added to waste streams to dissolve relatively insoluble materials such as dioxins. If not dissolved, the molecules of the compound are potentially protected from the ozone.

For waste streams with low concentrations of organics, ozonolysis/radiolysis is potentially an effective pretreatment technique. It can also provide effective control of air emissions in the vapor phase where the

TABLE 5-19. WASTE STREAM REQUIREMENTS FOR OZONATION/RADIOLYSIS

Characteristics	Processes not suitable for these characteristics (see Figure 5-13)	Processes suitable for these characteristics (see Figure 5-13)
High volatiles content	All	
1% < volatile content < 5%	A, C, E, D	B
Sludges	D	A, B, C
Opaque liquid	D	A, C

efficiency of photolysis is expected to be substantially enhanced (relative to liquids) radiation attenuation in the vapor state.

Potentially, ozone can destroy almost all volatile compounds, since the ultimate oxidation products are carbon dioxide and water. Cyanide can be converted to the cyanate or degraded to carbon dioxide by ozonation. Ammonia can also be converted to nitrate. Alcohols are converted to aldehydes and carboxylic acids. Phenols are converted to oxalic acid. Unsaturated hydrocarbons are fragmented and converted to aldehydes, ketones, and carboxylic acids (Berkowitz et al. 1978).

The use of ozone to reduce volatiles in hazardous waste streams can be accomplished by converting the volatile compounds to compounds which may be less volatile than the parent organic compound. Although the acid product is resistant to ozonation, the potential for environmental air emissions could be reduced. The use of photolysis with ozonation can promote the more complete oxidation to carbon dioxide.

Table 5-20 presents materials which are suitable for low energy photolysis. The process of photolysis is much more limited than the combined ozonation/radiation process.

Although ozone and photolysis together can destroy most oxidizable compounds, the kinetics and efficiencies of specific volatile destructions are not generally known. For this reason, pilot studies are required to determine the treatment costs using ozonation/photolysis for specific waste streams. The economics of a particular application should not be evaluated before obtaining this laboratory data. Ozone generation is the most expensive element in UV/ozonation pretreatment of hazardous waste. To decrease the cost of the ozone generation, ozone could be generated in situ, using UV radiation.

5.5.2.3 Waste Stream Laboratory Data--

Although hazardous waste treatment with ozonation/radiolysis has been demonstrated as effective for several specific waste streams, the laboratory testing covers only a very few waste streams. Using a mixture of carbon tetrachloride and water, 97 percent destruction of dioxin was obtained with ozone treatment (Cavolloni and Zecca 1977). Apparently the carbon tetrachloride permits the solubility of the 2, 3, 7, 8-TCDD, which is necessary

TABLE 5-20. MATERIALS SUITABLE FOR LOW ENERGY (UV) PHOTOLYSIS[a]

	Suitable	Unsuitable
By Physical Form of Waste		
	Gases Aqueous solutions Nonaqueous solutions Clear liquids	Slurries Sludges Tars
By Chemical Nature of Contaminants		
Inorganics	Cyanides Carbonyls	Heavy metals Fluorides Acids
Organics	Aromatic hydrocarbons Aromatic amines Aromatic alcohols Aromatic ethers Halogenated aromatics Nitro and nitroso compounds Phosphorous and sulfur pesticides	Aliphatic hydrocarbons Chlorinated aliphatics Aliphatic alcohols Aliphatic ethers Aliphatic amines Aliphatic acids

[a] Source: Berkowitz et al. 1976.

for the destruction. Houston Research Incorporated treated dioxins with ozone combined with ultraviolet radiation. The decomposition products were carbon dioxide, water, and hydrochloric acid (Wilkinson et al. 1978). The decomposition of ozone was accelerated by the use of ultraviolet radiation.

The Pittsburgh Energy Technology Center has examined ozonolysis as a treatment technique for processing wastewater. Cooling tower wastewater has been treated with ozonation, although the primary objective was to reduce the blowdown, since ozone can make the inorganic materials more soluble.

Dipak (1984) developed a laboratory bench-scale apparatus for investigating the treatment of waste materials with ozone and photolysis. Approximately 60 minutes retention time was required for 70 to 80 percent conversion of a wood preservative waste stream that had a COD of between 40,000 to 50,000. The 3-liter reactor was irradiated by an 8 watt UV source within an enclosed quartz tube. Approximately 0.8 lb per day of ozone was applied to the reactor. There was another benefit to ozonation other than oxidation. Only 10 minutes processing in the ozone/photolysis reactor was required to improve the settling separation process.

Three commercial organizations have direct experience in pilot and full-scale operation of photo oxidation procedures of industrial waste streams (Berkowitz et al. 1978). Dow Chemical, with joint funding from EPA, has developed a UV-chlorination process to remove acetic acid from 200 gpm of a brine stream. The acetic acid is oxidized to CO_2 and CH_3Cl by a combination of Cl_2 and irradiation. This facility has been in use for over a year and consistently achieves better than 90 percent acetic acid removal with residence times of 1 hour. The process was considered at least competitive with carbon absorption for acetic acid removal. Houston Research, Inc., developed UV/Ozonolysis treatment units for oxidation of refractory materials such as complexed cyanides, organic nitrogen compounds and acetic acid. Because of the synergistic effect with ozone, the addition of UV radiation enhances the rates of conversion 10^2 to 10^4 fold. Facilities capable of treating 100 gpm have been installed, with removal efficiencies of > 90 percent with residence times 0.5 to 1 hour. The total organic carbon is reduced in concentration; complete conversion to CO_2, H_2O, etc., was expected. The Velcicol Chemical Corporation proposed a photolytic system for the disposal of herbicide Orange (Esposito et al. 1980). Butyl alcohol would be used to extract the dioxins and irradiated by UV light. The process was not developed further, because the toxicity of the byproducts of 2,3,7,8 TCDD destruction was unknown. There was no mention whether the oxygen concentration was controlled in other laboratory studies, perhaps explaining contradictory results in various laboratories.

High energy radiation such as gamma rays have been used to destroy dioxins in oxygenated solvents. As in the low energy radiation results, oxygen effects could account for incomplete conversions in some of the laboratory studies.

5.5.3 Example Case

Figure 5-14 presents a flow diagram of a model pretreatment facility for removing benzene, toluene, and phenol from quench tower blowdown from ethylene production by cracking of heavy liquids. This stream is a high volume (426,000 kg/day each unit) containing benzene. Most applications of ozonation processes are generally of much smaller scale than this example, and would not have the complexity of an oxygen plant.

The costs and energy requirements for the ozone pretreatment facility are presented in Table 5-21. Because of the enhanced oxygen content, the energy required for ozone generation is less than if the generator were operating with air.

The reactor vessel and the offgas reaction chamber have UV lamps installed within the reactors. The ozone is generated by the lamps at a relatively low concentration since the reaction rates are expected to be much faster in the vapor than in the liquid. Some volatiles are expected to be oxidized by ozone diffusing into the liquid, however.

5.5.4 Advantages and Disadvantages

The advantages and disadvantages of ozonation/radiolysis are summarized in Table 5-22. One of the main disadvantages is that the technology has not been examined in detail for some of the more potentially cost effective waste pretreatment techniques, such as air stripping followed by reaction of the volatile offgases in a UV chamber.

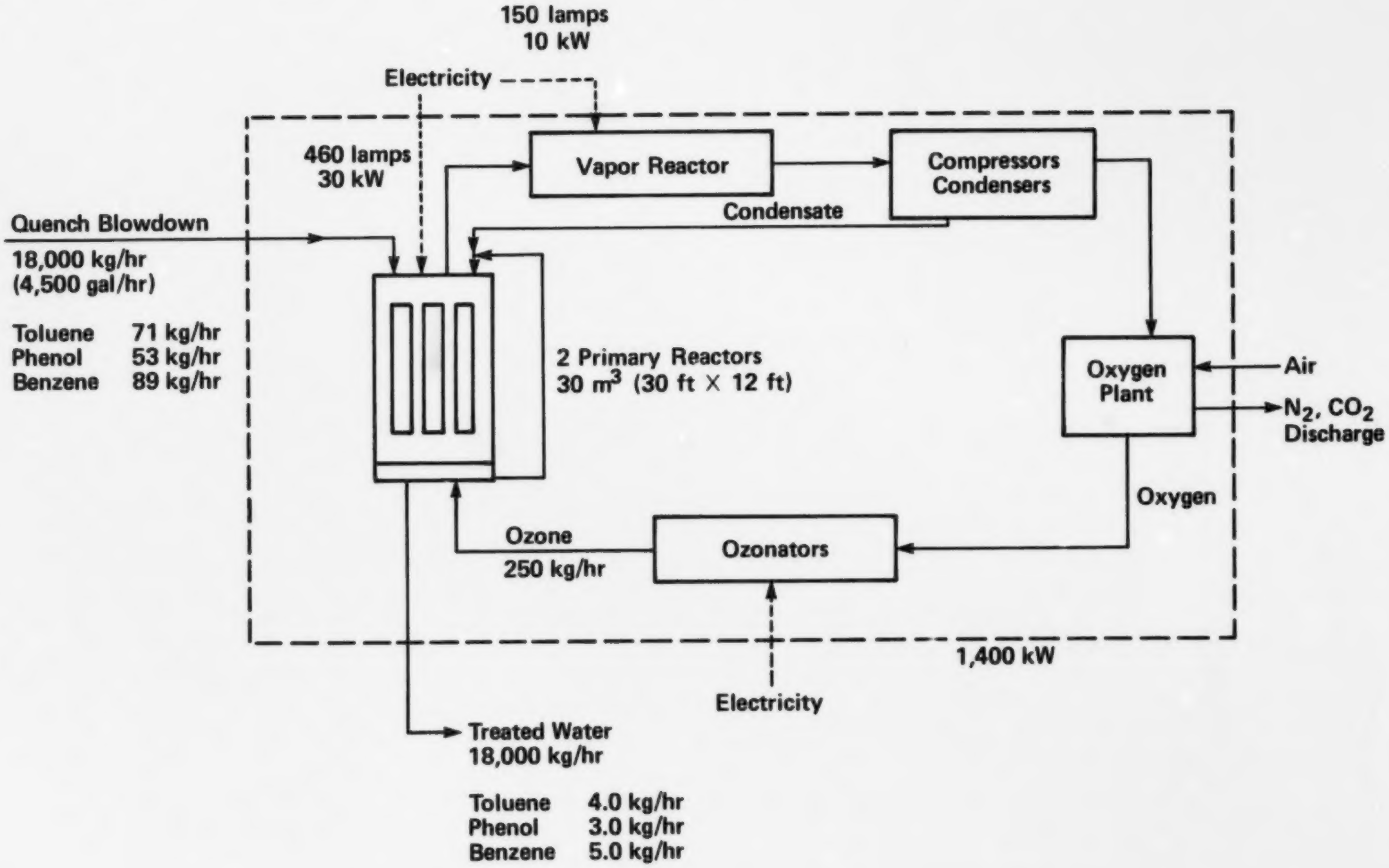

150 lamps
10 kW
Electricity
460 lamps
30 kW
Vapor Reactor
Compressors
Condensers
Condensate
Quench Blowdown
18,000 kg/hr
(4,500 gal/hr)
Toluene 71 kg/hr
Phenol 53 kg/hr
Benzene 89 kg/hr
2 Primary Reactors
30 m³ (30 ft X 12 ft)
Oxygen
Plant
Air
N₂, CO₂
Discharge
Oxygen
Ozone
250 kg/hr
Ozonators
1,400 kW
Electricity
Treated Water
18,000 kg/hr
Toluene 4.0 kg/hr
Phenol 3.0 kg/hr
Benzene 5.0 kg/hr

Figure 5-14. Process flow sheet for ozonation pretreatment of quench blowdown from ethylene production by cracking of heavy liquids.

TABLE 5-21. OPERATING COSTS (1980$) AND ENERGY REQUIREMENTS FOR OZONE GENERATION

Process	$ or energy
610 Lamps 65 W	40 kW
Lamp replacement	$43/day[a]
Monitoring labor	$85.71[a]
Reactor	$250,000[b]
Ozone generator/oxygen plant 250 kg/h	$8,000,000[c]
Ozone generator electricity	$1,400 kW
Maintenance/operation 2 men total system	$200,000/year

[a] Arisman and Musich (1980).

[b] Twice the reactor cost in Arisman and Musich (1980) plus 40 percent for contingencies.

[c] Air Products, Allentown, PA (1984).

TABLE 5-22. OZONATION/RADIATION

Advantages:

1. Destroys a wide variety of organic materials.
2. No harmful residues associated with the ultimate products.
3. Efficient removal of trace quantities of organics.
4. Effective destruction of organics in the vapor phase.
5. Can selectively modify waste composition for some pretreatment applications.
6. Can serve as a final treatment for some wastes.
7. Systems can be fully automated.
8. Can be used as a portable system.

Disadvantages:

1. Not a demonstrated technology for many waste streams.
2. Viscous streams would be difficult to process.
3. UV radiation only penetrates the surface of opaque liquids and sludges.
4. Expensive for purifying concentrated organic wastes (greater than 1 to 2 percent).
5. Byproducts can be potentially toxic if the oxidation is incomplete.
6. Does not selectively remove volatiles, all oxidizable compounds can potentially react with the ozone.

One major advantage of ozonation is that the process leaves no harmful residue. Ozone decomposes naturally in water with a half-life of approximately 25 minutes. This decomposition time is reduced when reactive organics are present. Ozonation systems are relatively compact. This makes ozonation an attractive addition for retrofit considerations. (De Renzo 1981).

5.5.5 Recommendations for Further Study

Since the conversion of oxygen to ozone by UV light is more effective when organics are present and the UV light can uniformly irradiate the vapor space, air stripping of the waste material at ambient temperatures, followed by UV radiolysis of the resulting vapors is a potentially attractive alternative process. The electrical efficiency of such a process is expected to be substantially improved over a process which requires an external ozone generator.

The use of the zeolite pressure swing oxygen enrichment technology for improving the efficiency of ozone production should be examined. Up to 95 percent oxygen can be obtained with such a system. This would potentially permit both lower capital costs and lower electrical costs. The low moisture requirements of the zeolite beds are compatible with the low moisture requirements of the ozone generator.

5.6 DISTILLATION

5.6.1 Introduction

Distillation is a well established process that effects component separation based upon differences in volatility. This process has been an inherent part of the chemical and petroleum industries for many years. Distillation typically involves heating a feed mixture to produce liquid and vapor phases; the more volatile constituents of the feed concentrate in the vapor phase, while the less volatile components concentrate in the liquid phase.

Distillation is routinely used to separate volatile compounds that are considered hazardous from an environmental standpoint. For example, the ethylbenzene/styrene industry routinely separates benzene and toluene by distillation. Pretreatment of waste streams by distillation will, in most cases, involve the same distillation process that is commonly used to separate valuable chemicals in the chemicals manufacturing industry. Thus, in many cases, established distillation procedures are applicable for the pretreatment of volatile waste streams.

5.6.2 State of the Art

Distillation has evolved into a process that is conducted primarily in one of the two possible modes, namely the batch or continuous modes. Most large-scale industrial applications utilize continuous distillation (Berkowitz et al. 1978); however, batch distillation can prove to be advantageous in some situations. These two modes of operation are discussed in Sections 5.6.2.1 and 5.6.2.2, respectively.

5.6.2.1 Continuous Distillation--

Continuous distillation involves the uninterrupted (continuous) introduction of a feed stream(s) to an appropriately designed distillation column. Such a scheme is illustrated in Figure 5-15. The feed stream is fed to a column that contains plates or packing [packing is normally used only in small-scale equipment (Berkowitz et al. 1978)] designed to provide intimate contact between vapor and liquid. If only one feed stream is involved, the cascade (set of plates) above where the feed stream is introduced to the column is termed the rectifying or enriching section of the column, while the cascade below the feed stage is termed the stripping section. Vapor rising through the rectifying section of the column is washed with liquid to remove the less volatile components, while the liquid in the stripping section of the column is "stripped" of the more volatile components by the rising vapor in that section. A condenser is used to condense the overhead vapor that exits the rectifying section of the column. A portion of this condensate is continuously withdrawn as the overhead product, while the remainder of the condensate is returned to the column as reflux. At the bottom of the column, liquid that exits the stripping section is collected in a reboiler where it is heated to produce a vapor stream that is returned to the column. The portion of the liquid that is not vaporized and returned to the column is continuously withdrawn as the bottoms product.

Distillation columns for continuous operation may be designed to handle multiple feed streams (McCabe and Smith 1976); however, continuous

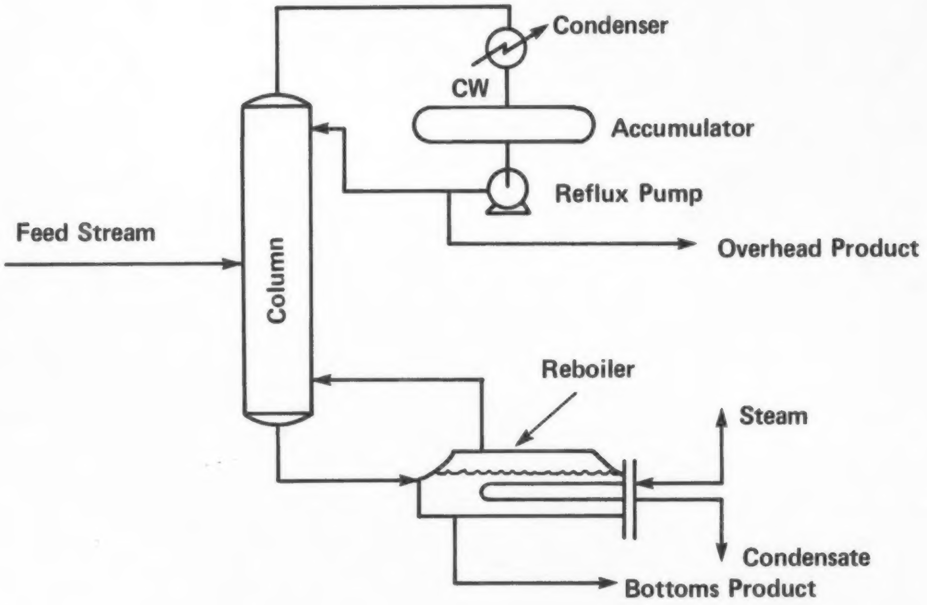

Condenser
CW
Accumulator
Reflux Pump
Overhead Product
Feed Stream
Column
Reboiler
Steam
Condensate
Bottoms Product

Figure 5-15. Process flow sheet for continuous fractional distillation column.

distillation, even with multiple feeds, typically requires that the feed streams do not vary significantly in composition with time. This is due to the fact that continuous distillation systems do not accomodate frequent fluctuations in feed stream composition while maintaining the overhead and bottoms products at the levels of purity specified in the design. Continuous operation is also hampered by frequent startups and shutdowns.

5.6.2.2 Batch (Differential) Distillation--

Batch or differential distillation entails distilling the feed material in batches rather than continuously. There are two basic types of batch distillation systems, namely:

- Simple batch distillation systems
- Batch distillation systems utilizing rectification

Simple batch distillation is illustrated in Figure 5-16. It consists of a heated vessel (the "still" or "pot"), a condenser to condense the overhead vapor, an accumulator (a necessity if reflux is employed), and several receiving vessels to collect the overhead and bottoms products. Operation envolves charging a batch of feed to the still with subsequent boiling of the feed mixture. The overhead vapor stream is condensed and collected in an appropriate receiving vessel. Reflux (returning some of the condensed overhead product to the still) may or may not be employed, depending upon the desired product composition. Use of simple batch distillation is usually restricted to preliminary separations where the products are held for additional separation at a later time.

In most batch distillation operations, the compositions of the overhead and bottoms products will vary in composition as the distillation proceeds. In the absence of reflux or at a constant reflux ratio, the overhead product will become progressively richer in the less volatile components while the residual liquid or bottoms becomes progressively leaner in the more volatile components. Thus, depending upon the planned ultimate fate of the products, either the overhead product composition or the bottoms product composition may dictate the extent to which the distillation process is carried out.

To obtain products within a narrower composition range, batch distillation with rectification may be used (Perry and Chilton 1973). The compon-

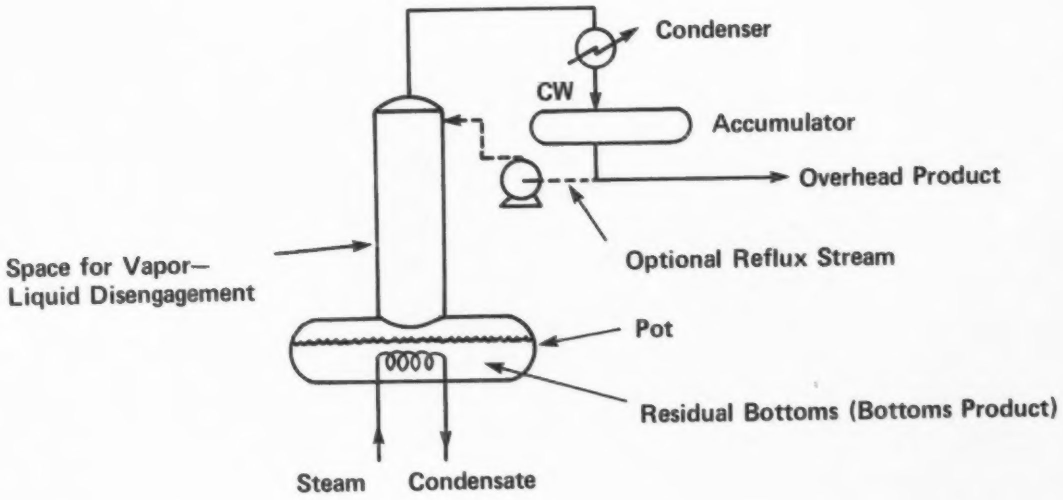

Condenser
CW
Accumulator
Overhead Product
Optional Reflux Stream
Space for Vapor—
Liquid Disengagement
Pot
Residual Bottoms (Bottoms Product)
Steam
Condensate

Figure 5-16. Process flow sheet for simple batch distillation scheme.

ents of this system are the pot, a rectifying column, a condenser, a splitter for returning a portion of the distillate as reflux, and one or more product-receiving vessels. This setup is illustrated in Figure 5-17. In operation, a batch of feed is charged to the pot, and the system is brought to steady state under total reflux conditions. Once steady state is achieved, removal of some of the overhead product (that amount not returned to the column as reflux) is commenced. Some degree of control over the overhead product composition can be achieved by appropriate adjustment of the reflux ratio as the distillation proceeds. Two primary modes of operation are the following (Perry and Chilton 1973):

- Constant reflux ratio with varying overhead composition
- Constant overhead composition with varying reflux ratio.

Under the first mode, distillation is conducted under a constant, predetermined reflux ratio until the average distillate composition reaches the desired value. At this point, the overhead is diverted to another receiving vessel, and an intermediate cut is withdrawn until the liquor remaining in the pot reaches the desired composition.

The second mode, constant overhead composition, can be maintained by constantly increasing the reflux ratio as the run proceeds. At a point where the reflux ratio reaches a very high value, the overhead is diverted to a different receiving vessel, and the reflux ratio is decreased. An intermediate cut is then taken as before to achieve the desired composition in the residual liquid.

5.6.2.3 Status of Commercial Development--

Both batch and continuous distillation have been practiced on a commercial scale for many years (Berkowitz et al. 1978). Very often in the production of organic chemicals, the products are not in a pure state. Distillation is frequently used to separate products from secondary byproducts. In fact, distillation is routinely used to separate volatile compounds that are considered hazardous from an environmental standpoint.

Distillation is an energy intensive process. Consequently, most applications to date involve the recovery of soluble or recyclable species (Berkowitz et al. 1978). For example, chemical manufacturers recover

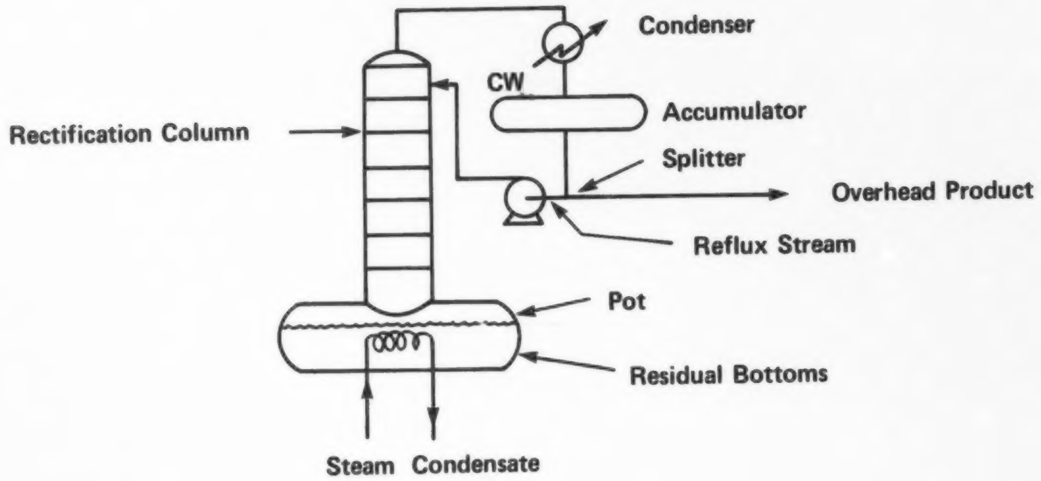

Condenser
CW
Accumulator
Rectification Column
Splitter
Overhead Product
Reflux Stream
Pot
Residual Bottoms
Steam
Condensate

Figure 5-17. Process flow sheet for batch distillation with rectification.

solvents via distillation for internal reuse. Due to the high cost, pretreatment and treatment of wastes by distillation is not widespread.

There are, however, a number of independent operations that specialize in solvent and chemical reclamation by distillation. Table 5-23 presents a partial listing of independent processors and waste solvent distillers.

5.6.2.4 Constraints and Restrictions--

There are several important constraints on the physical form and chemical nature of wastes that are to be treated by distillation. Tables 5-24 and 5-25 present forms and types of wastes that are amenable to pretreatment by distillation. One primary constraint is that the feed to a continuous distillation column must be a free flowing fluid with negligible solids content. Solid materials will severely plug and foul the internals of the column. If the waste stream does contain solids or highly viscous liquids, some form of prior conditioning will be required. There are, however, some free flowing fluids that cannot be treated by distillation. These include organic peroxides, pyrophoric organics, and most inorganic wastes.

The hazardous waste streams that are best suited for volatiles removal/ reclamation using distillation are liquid organics, including organic solvents and halogenated organics. Typical industrial wastes that can be handled by distillation include the following:

- Plating wastes containing an organic component--usually the solvents are evaporated and the organic vapors distilled.
- Aqueous wastes containing phenol.
- Polyurethane waste containing methylene chloride.
- Ethylbenzene/styrene mixtures.
- Waste solvents--usually mixtures containing ketones, alcohols, and aromatics.
- Waste lubricating oils
- Waste containing butyl acetate that are produced via antibiotics (penicillin) manufacture

As suggested in Section 5.6.2.1, continuous distillation is not well suited for wastes that exhibit large and/or frequent variations in composi-

TABLE 5-23. PARTIAL LISTING OF INDEPENDENT PROCESSORS AND WASTE TREATMENT DISTILLERS[a]

Chemical Exchange Company
Houston, TX

CPS Chemical Company
Old Bridge, NJ

Chemical Processor, Inc.
Seattle, WA

Conservation Chemical Company
Kansas City, MO

Waste Research and Reclamination Co., Inc.
Eau Claire, WI

Rodgers Laboratories, Inc.
Milwaukee, WI

Chemical Waste Disposal Corporation
Astoria, NY

Chem-Trol Pollution Service Inc.
Subsidiary of SCA Services Inc.
Model City, NY

National Convertors, Inc.
Union, NJ

Marisol, Inc.
Middlesex, NJ

Silresim Chemical Corporation
Lowell, MA

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[a] Source: Berkowitz et al. 1978.

TABLE 5-24. WASTE FORMS THAT CAN BE DISTILLED

Waste form	Yes	No	Remarks
Aqueous liquids	✓		
Aqueous vapors	✓		
Organic liquids	✓		
Organic vapors	✓		
Gases	✓		
Slurries	✓		
Sludges	✓		After some form of pretreatment
Tars		✓	
Solids		✓	
Dry powders		✓	

TABLE 5-25. WASTE TYPES THAT CAN BE DISTILLED

Waste type	Yes	No	Remarks
Inorganics		✓	Possibly some exceptions, but these would not be relevant or practical to hazardous waste pretreatment or to its reclamation.
Organics:			
Plain hydrocarbons	✓		
Halogenated hydrocarbons	✓		
Amines	✓		
Nitro compounds		✓	These are all general cases; there may be some exceptions to the rule.
Explosives		✓	
Oxygenated hydrocarbons	✓		
Sulfur-containing organics	✓		
phosphorus-containing organics	✓		
Lead containing organics	✓		

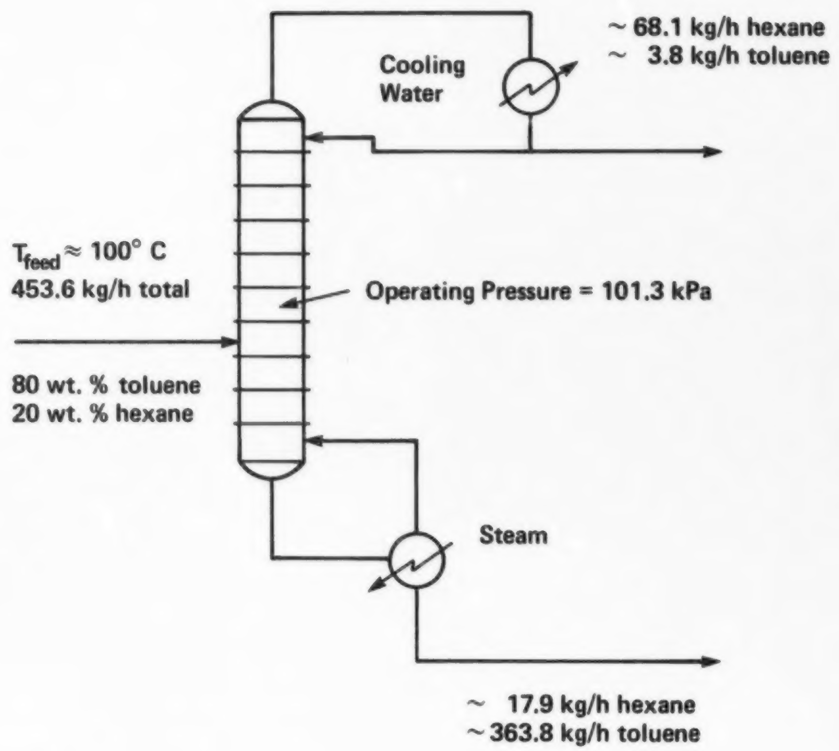
tion. This is primarily due to the complexity of the process dynamics involved, i.e., the distillation column's ability to respond to fluctuations in feed stream composition so as to maintain the desired overhead and bottoms compositions. Batch distillation setups are, on the other hand, used quite frequently in applications where mixtures of widely varying composition are to be distilled. As mentioned in Section 5.6.2.2, careful regulation of the reflux ratio can be used to exercise control over the overhead product composition. In addition, the charge to a batch unit may also be high in solids content, or it may contain tars or resins that would plug or foul a continuous unit (Perry and Chilton 1973). Such materials merely settle out in the pot and are conviently removed at the termination of the process. It is still desirable, however, that the bulk of the feed consists of a free flowing fluid.

Batch operation, by its very nature, involves frequent startup and shutdown. Thus, an irregular supply of waste should present no problem in as far as forcing undesired startups and shutdowns that would tend to cause operational problems for a continuous unit.

It is essential to note that treatment by distillation will serve only to reclaim volatiles in a more concentreated form. In addition, process residuals such as still bottoms may present a waste disposal problem. If volatiles can be recovered at desirable concentrations, it is likely that many could be sold. Otherwise, ultimate destruction/disposal via a means by which volatile emissions can be avoided will be required. Solids, tars, or sludges recovered from still bottoms are normally incinerated (Berkowitz et al. 1978). It is thus evident that the ultimate fate of some distillation products may present another form of waste disposal problem, i.e., that of disposing of concentrated volatile matter and/or other residuals produced by the distillation process.

5.6.3 Example Case

Preliminary capital and operating cost estimates have been developed for a continuous distillation unit designed to treat 1000 lb/hr of spent solvents (primarily hexane and toluene). This feed stock roughly corresponds to stream 03.01.90 to the WET Model Data Base. A flow sheet for this process (including material balances) is presented in Figure 5-18. The design basis is as follows:



~ 68.1 kg/h hexane
~ 3.8 kg/h toluene
Cooling Water
$T_{feed} \approx 100°$ C
453.6 kg/h total
Operating Pressure = 101.3 kPa
80 wt. % toluene
20 wt. % hexane
Steam
~ 17.9 kg/h hexane
~ 363.8 kg/h toluene

Figure 5-18. Process flow sheet for example case of distillation pretreatment.

- Feed rate of 1000 lb/hr spent solvents (80 percent toluene, 20 percent hexane).
- An overhead product composition of 95 percent hexane, 5 percent toluene.
- A bottoms product composition of 5 percent hexane, 95 percent toluene.
- The feed to the column is saturated liquid, i.e., liquid at its bubble point.
- Column operation is at atmospheric pressure.

It was determined by engineering estimate that a bubble cap tower containing 10 stages would be adequate to effect the desired separation. Column diameter was estimated to be 1 foot. A total condensor was specified, along with a "coffin still" type kettle reboiler.

Under the assumption of 2800 hours per year operation, the overhead product would be produced at about 80,958 gal/yr, while the production of bottoms product would be about 327,400 gal/yr. It has been assumed that the volatile stream could be sold for $0.10/kg.

The total capital cost for this scenario (including direct, indirect, and contingency costs) was estimated to be $352,500 (January 1983 dollars). Similarly, total annual operating expenses (including byproduct recovery credit) were estimated to be $6,225/yr. Discounting the capital cost at 10 percent over 10 years results in a total annualized cost of $63,683/yr. The unit cost is estimated to be $0.05/kg of waste treated. For disposal of volatiles that cannot be recycled, steam stripping may be used for additional purification or, for ultimate disposal, incineration.

5.6.4 Advantages and Disadvantages

The primary advantages and disadvantages associated with distillation are summarized as follows:

5.6.4.1 Advantages--

- Distillation is capable of recovering volatile species without concomitant degradation. This is an important advantage when the recovered species can be sold or recycled.

- Product purity of any desired level can be obtained, at a cost.

5.6.4.2 Disadvantages--

- Distillation systems cannot handle feeds having high quantities of solids, tars, or feeds that tend to polymerize without suffering severe operational difficulties unless the streams can be pretreated to reduce or remove these materials.

- Equipment and auxiliaries are usually comparatively large. They can have heights up to 200 ft and cover large areas.

- The equipment is expensive, and capital recovery charges usually constitute the major portion of solvent recovery cost.

- Recovery by distillation is energy intensive. Energy requirements are nominally 250 to 1,200 Btu/lb of feed.

- Equipment is often complex and requires operation by highly skilled personnel.

- Still bottoms sometimes contain tars and sludges which must be disposed of in landfill or by incineration.

5.6.5 Recommendations for Further Study

Since distillation is a well developed technology, recommendations for further study involve determining which modes of operation might be best suited for the pretreatment of waste streams. For instance, distillation can be conducted under special conditions that modify the phase equilibrium behavior of the species involved in order to enhance separation. Such methods include:

- Operation at reduced pressure
- Azeotropic distillation
- Extractive distillation

The adoption of any of these schemes will affect cost substantially (compared to straightforward distillation at atmospheric pressure), and thus should be considered carefully. An assessment of the type of distillation conditions (as enumerated above) required to effectively process large volume wastes would reveal a great deal about the overall economic viability of distillation for waste stream pretreatment.

For specific applications, the choice between batch and continuous distillation should also be studied carefully. As noted in Section 5.6.2.2, there are some circumstances under which batch distillation may be favorable even though it is considerably more difficult to maintain the composition of the products at a constant level. Batch distillation may be preferred when:

- The composition of the feed varys significantly.
- The feed contains significant amounts of solids that would tend to foul and plug a continuous unit.
- Excessive startup/shutdown might be required due to an irregular supply of the feed.

In summary, distillation (either batch or continuous) tends to be energy-intensive and thus expensive unless the product can be recycled or sold. However, with sufficient byproduct credits, it can sometimes compete with processes having a much lower capital recovery cost. It should be noted that when distillation is competitive on an economic basis, it generally becomes the preferred method of recovery where salable organic species are involved (Berkowitz et al. 1978).

5.7 WET OXIDATION

5.7.1 Introduction

Wet oxidation is a process in which oxidizable material present in aqueous solution or suspension is reacted with oxygen in the liquid phase. This process is used either for energy recovery or for wastewater treatment, depending on the composition of the aqueous stream. The reaction is typically conducted at elevated temperatures to accelerate the reaction and elevated pressures to maintain the reaction medium in the liquid phase and increase the solubility of oxygen. The pressurizing gas can be air or oxygen.

The wet oxidation process is applicable to aqueous streams contaminated with organics. It is particularly suited to waste streams that are available at elevated temperatures and pressures. Generally, the more concentrated the stream, the greater the benefits of wet oxidation; however, extremely concentrated streams (sludges and pastes) may be more economically incinerated even though they are primarily aqueous. Although most organic components, including those responsible for volatile emissions, can be oxidized to some extent, the suitability of particular waste streams for the process can be confirmed through relatively simple bench-scale testing.

5.7.2 State of the Art

5.7.2.1 General Process Description--

The aqueous waste stream is pumped to a boiler, where compressed air or compressed oxygen is added. The high partial pressure of oxygen increases the concentration of dissolved oxygen in the aqueous phase. Reaction takes place between the dissolved oxygen and the dissolved (typically organic) compounds in the liquid phase. Additionally, suspended carbonaceous material will also combine with dissolved oxygen. These reactions are exothermic; if enough oxidizable material is present in the waste stream to offset heat losses, a net energy recovery may be obtained. Heat from the treated wastewater leaving the boiler is exchanged with the entering wastewater in order to elevate it to reaction temperature.

The reaction typically is conducted at temperatures between 150° and 300° C with total pressures somewhat higher than the saturation pressure of water at the temperature chosen. Total pressures are typically in the range of 10 to 70 atmospheres. Depending on the species to be oxidized, catalysts can be added to increase reaction rates and decrease required vessel volumes (residence times).

As operating experience with this technology for waste treatment is limited, wet oxidation should be regarded as an emerging technology rather than an established one. It is, however, being aggressively marketed by at least three companies: Zimpro (Rothschild, Wis.); IT Enviroscience (Knoxville, Tenn.); and Wetcom Engineering (Toronto, Ontario).

Laboratory and pilot-scale research for wet oxidation treatment of organically contaminated aqueous solutions has increased in recent years. Table 5-26 lists recent research efforts in this area. In addition to the original patent on the Zimmerman process (Zimmerman 1958), process variations have been patented by Burke and Borswinkle (1974) and Dow Chemical Co.

TABLE 5-26. RECENT RESEARCH ON THE APPLICATION OF WET OXIDATION TO AQUEOUS WASTE STREAMS

Waste stream or waste stream component	Reference:
Waste sulfate liquor	Pradt (1972)
Coke-oven gas-scrubber liquor, coal gasification condensate, sulfide refinery spent caustic, DDT, cyanide wastes from electroplating, and wood preservative liquor	Laughlin (1983)
Coal gasification condensate	Green et al. (1983)
Dichloronitrobenzoic acid herbicide and coke plant waste	Adams et al. (1976)
Phenol	Katzer et al. (1976); Pruden et al. (1973); Sadana and Katzer (1974); Sadana (1979); Njiribeuko et al. (1978); and Ohta et al. (1980)
Phenol, coal gasifer condensate, oil refinery wastewater and adhesives and sealant wastewater	Bansel et al. (1978)
Phenol and nitrilotriacetic acid	Pruden et al. (1976)
Ten different solutions of pure organic compounds	Randall and Knopp (1980)
Phenol, naphthalene, and biological waste treatment sludge	Harris et al. (1983)

5.7.2.2 Process Details--

A simple process flow sheet for wet oxidation is shown in Figure 5-19. This schematic shows the process as operated for wastewater treatment only. In some cases, an externally heated preheater is required to initiate the reaction; for dilute streams (<1 percent COD) supplemental heat may be required to maintain appreciable reaction rates.

The key design variables are residence time and pressure. These can be determined by bench scale testing of the actual waste stream. In addition the effects of various heterogeneous and homogeneous oxidation catalysts can be determined at bench scale to evaluate the benefits (in terms of reduced vessel size) and costs of these materials.

Where energy recovery is feasible, and turbines are added for steam expansion, the plant becomes more complicated. A schematic of this type of plant is shown in Figure 5-20. A mass balance for treatment of Amiben® wastewater based on Adams et al. (1976) is given in Table 5-27.

The possibility exists for volatile organics to evolve from pretreated aqueous streams since treated streams may be discharged at elevated temperatures. In addition, some components may be stripped from the aqueous phase into the reactant air and require exhaust-gas controls after the pressure is reduced. In some process variations, catalysts are added. Ultimately these catalysts must be replaced or regenerated, at which time they may become solid wastes or produce emissions when the catalysts themselves are regenerated.

The wet oxidation process produces no sludges or solid wastes. The destroyed components are either completely converted to carbon dioxide or partially oxidized to other soluble, presumably less volatile, components.

5.7.2.3 Existing Sites--

Pradt (1972) has reported that there are over 150 wet oxidation installations world-wide, including 12 units that treat pure industrial waste, only one of which is in the United States. The remaining units include plants operated primarily for energy recovery rather than waste treatment. The process is said to be suitable for energy production from such low-grade, high-moisture carbonaceous solids as wood waste, municipal sewage sludge, and coal refuse (Pradt 1978).

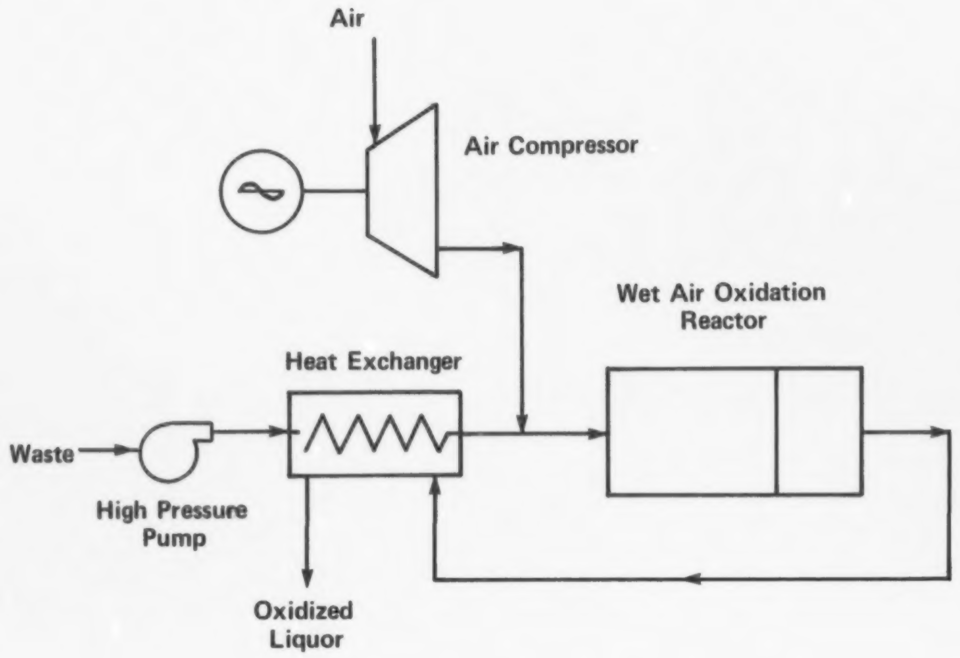
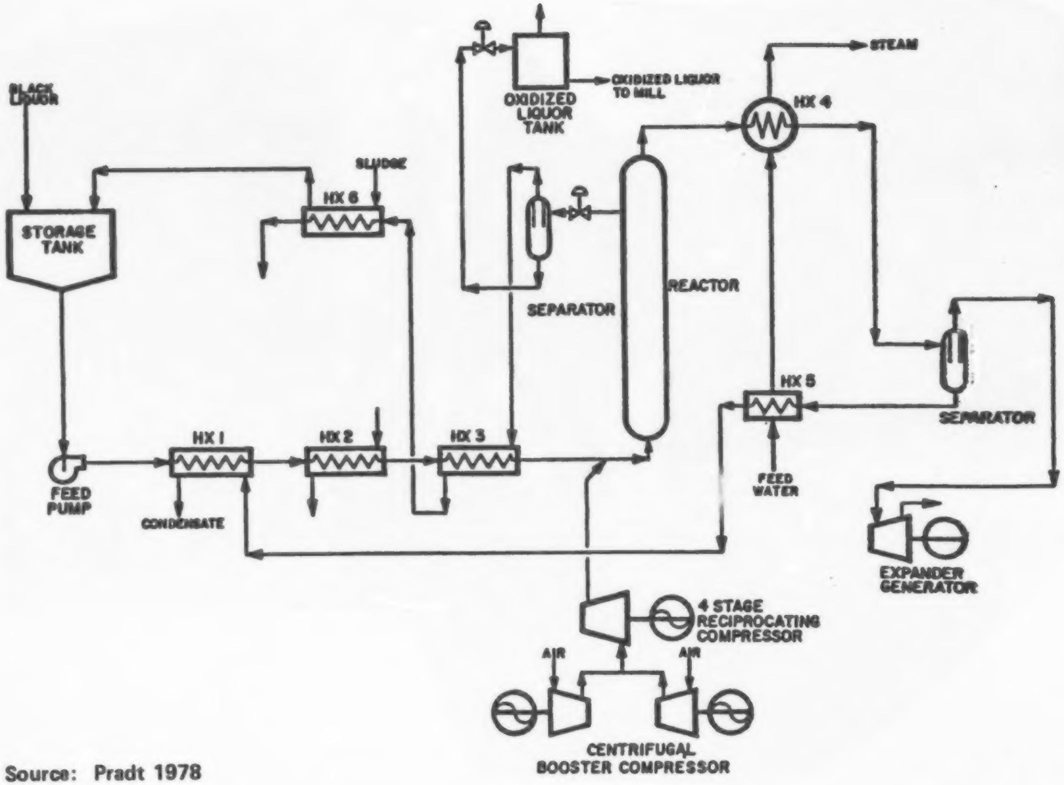

Air
Air Compressor
Wet Air Oxidation Reactor
Heat Exchanger
Waste
High Pressure Pump
Oxidized Liquor

Figure 5-19. Basic process flow sheet for wet oxidation.


BLACK LIQUOR
STORAGE TANK
SLUDGE
HX 6
OXIDIZED LIQUOR TANK
OXIDIZED LIQUOR TO MILL
STEAM
HX 4
SEPARATOR
REACTOR
HX 5
SEPARATOR
FEED PUMP
HX I
HX 2
HX 3
CONDENSATE
FEED WATER
EXPANDER GENERATOR
4 STAGE RECIPROCATING COMPRESSOR
AIR
AIR
CENTRIFUGAL BOOSTER COMPRESSOR

Source: Pradt 1978

Figure 5-20. Wet air oxidation plant for Hoerner, Waldorf, Ontonagon, Michigan.

TABLE 5-27. MASS BALANCE FOR WET OXIDATION TREATMENT OF AMIBEN® WASTEWATER

IN:	
Wastewater	40,000 gal/day
19.1 g/L Dichloronitrobenzoic Acid	
30.5 g/L COD	
Air (100% excess)	87,600 lb/day
OUT:	
Treated Wastewater	40,000 gal/day
<0.1 g/L Dichloronitrobenzoic acid	
2.92 g/L COD	
Gas	
Nitrogen	67,251 lb/day
Oxygen	11,100 lb/day
CO_2	12,600 lb/day
Gaseous hydrocarbons	140 lb/day
Carbon monoxide	280 lb/day

Source: Adams et al. 1976.

Several commercial plants have used the wet oxidation process. In Ontonagon, Mich., a plant was operated for Hoerner Waldorf Paper Company to oxidize waste pulping liquor. This stream contains about 12 percent solids making it suitable for energy recovery. It operates at a maximum temperature of 593 K at 20.0 MPa (Pradt 1978). The same type of waste stream was also treated commercially in Norway and again, energy recovery was the primary goal (Pradt 1978).

In 1972, a commercial installation of the Wetox® process, with a capacity of 50,000 L/day of industrial waste, was installed in Ontario. The stream to be treated has a chemical oxygen demand (COD) of approximately 7 percent and contains complex sulfur, nitrogen, and chlorine compounds (Laughlin et al. 1983). This plant is presently operating successfully and process developers estimate a two-year payback period under design conditions due to savings in the cost for offsite disposal and activated carbon.

5.7.2.4 General Economics--

Pradt (1972) estimated that a 200 gal/min stream containing 5000 mg/L of BOD could be treated for $0.0053/gallon (1970 $). Adams et al. (1976) estimated that a coke plant waste stream of 560,000 gal/day could be treated for $0.037/gal operating cost with a capital investment of $12.3 million (1976 $) or $21.96/gal/day. An Amiben® wastewater stream of 40,000 gal/day was estimated to require a $2.2 million capital investment ($55.00/gal/day) and operating costs of $0.068/gal (1976 $). Katzer et al. (1978) estimated that treatment of 800,000 gal/day of coke plant waste would cost $0.00075/gal (1974 $).

5.7.3 Example Case

5.7.3.1 WET Stream Chosen--

Wet stream 02.02.21, "Acetophenone column separator from phenol production by cumene hydroperoxide" has been chosen. This stream contains 1 percent phenol in aqueous solution and has a mass flow rate of 3,000 kg/day.

5.7.3.2 Process Information--

A process flow sheet is given in Figure 5-21. A mass balance for this process is given in Table 5-28.

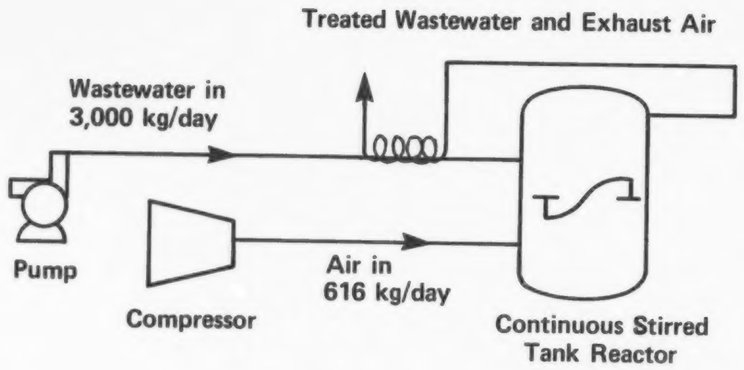

Treated Wastewater and Exhaust Air
Wastewater in
3,000 kg/day
Pump
Compressor
Air in
616 kg/day
Continuous Stirred
Tank Reactor

Figure 5-21. Process flow sheet for wet oxidation pretreatment of WET stream 02.02.21.

TABLE 5-28. MASS BALANCE FOR WET OXIDATION OF WET STREAM 02.02.21 (Acetophenone Column Separator from Phenol Production)

	kg/day
IN:	
Wastewater 10,000 mg/L phenol 23,800 mg/L COD	3,000
Air (100% excess)	616
OUT:	
Treated wastewater 1,000 mg/L phenol 7,000 mg/L COD	3,000
Gas	
Nitrogen	143
Oxygen	93
CO_2	69
Gaseous hydrocarbons	0.2
Carbon monoxide	1.5

5.7.3.3 Economics--

The WET model stream chosen has a relatively low volume and thus would be expensive to treat because of economies of scale cannot be achieved. A cost estimate has been prepared for a stream of 100 times this flow rate. This could be produced by collecting streams from various locations or mixing streams of similar composition (i.e., high phenol concentration) from other plant locations.

A plant to treat 300,000 kg/day of this stream could be built for an installed capital cost of approximately $8,200,000 (1983). Operating costs are estimated at $1.20/1,000 gallons of waste treated. This facility would remove approximately 1,000,000 kg/yr of phenol.

5.7.4 Advantages and Disadvantages

The advantage of wet oxidation is that it produces no sludges, solvents, or concentrated waste streams for disposal, and its space requirements are small. In addition, for some very concentrated wastes it may be practical to recover energy from the process.

The disadvantages of the process are that capital and operating costs may be high; this is due to the need for a pressure vessel (in which to conduct the reaction) and the cost of pumping and air compression. For streams containing very volatile but oxidation-resistant compounds, the vapor-phase emissions from the processed wastewater and effluent gas may require additional control measures.

5.7.5 Recommendations for Further Study

Individual bench-scale testing would be required to determine the suitability of wet oxidation as a pretreatment process for individual industrial wastes. In addition, testing to determine the optimal severity of the processing (i.e., residence times, temperature, and pressure) would be required for specific streams.

5.8 SOLVENT EXTRACTION

5.8.1 Introduction

Solvent extraction is a well-defined chemical engineering unit operation in which a solute is transferred from one liquid phase to a second immiscible phase. This transfer takes place when the solute is preferentially dissolved in one of two liquid solvents (i.e., at equilibrium, the concentration of the solute in one solvent phase is greater than the concentration of the solute in the other solvent phase). This difference in distribution of the solute between the two phases can be used to concentrate the solute in a smaller volume of solvent. The operation can be conducted as a batch process or by contact of the solvent with the feed in staged or continuous contact equipment.

The solvent extraction process is most suitable for the pretreatment of aqueous waste streams with high levels of organic constituents. The process is suitable for removal of valuable materials from waste streams since the organic contaminant is not destroyed in this treatment, but is simply transferred from the aqueous phase to the organic phase. This is advantageous for one or more of the following reasons:

- A smaller volume of waste to be treated is produced, i.e., the contaminant is removed from the original wastewater and is concentrated in the organic phase.
- If the organic phase is to be subsequently separated from the aqueous phase by distillation, less energy is required since the solvent has a lower heat of vaporization than the original wastewater.
- If the solvent is of little economic value and combustible, it can be incinerated more economically than the contaminated wastewater steam.

5.8.2 State of the Art

5.8.2.1 General Process Description--

The solvent and the wastewater are contacted in one or more stages and separated after each stage. The contacting takes place in an agitated vessel, and another vessel is used to permit separation of the phases by density differences. The two phases are pumped off separately and can be processed further in consecutive mixer/settlers. Flow is generally countercurrent in this operation.

Alternatively, continuous contact (generally countercurrent) can be achieved in vertical columns such as spray towers, packed towers, and sieve-plate towers. Spray towers are the simplest process: the lighter

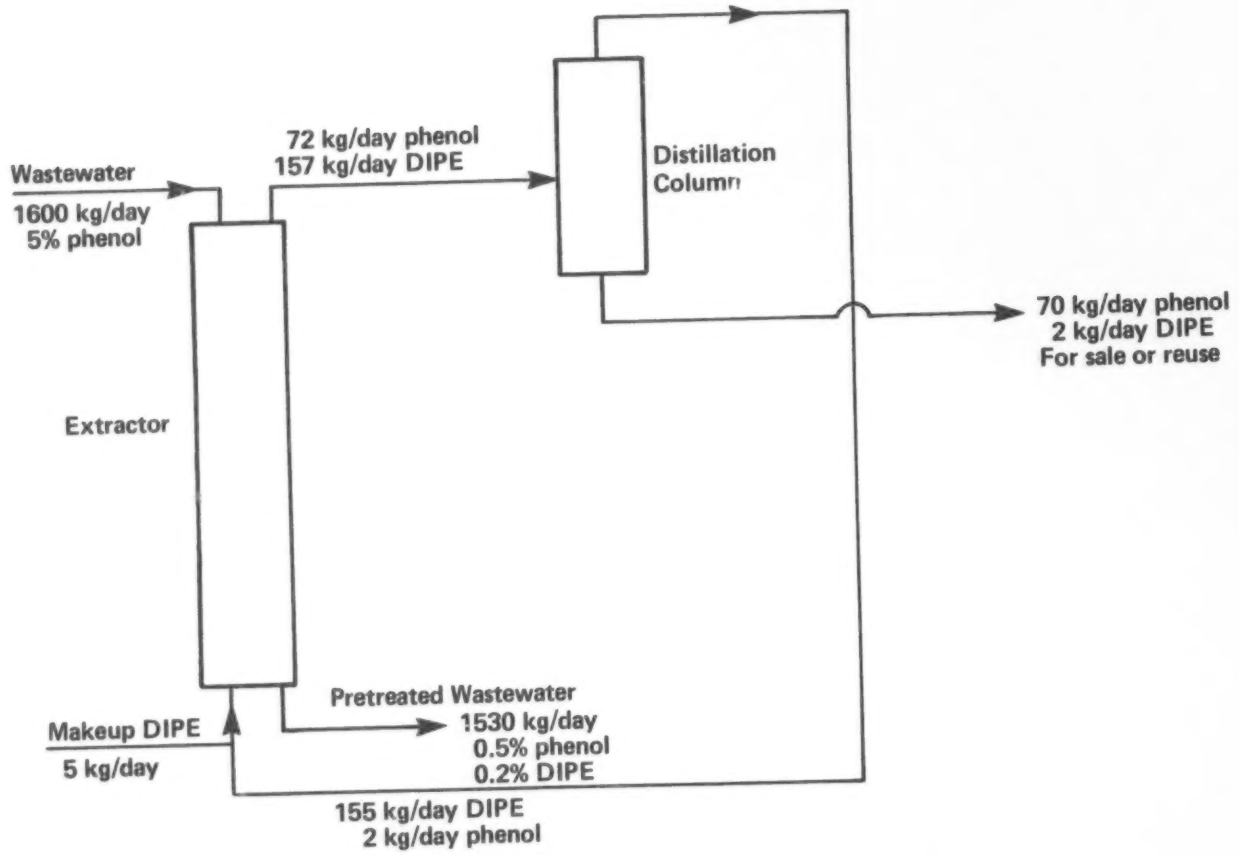

Wastewater
1600 kg/day
5% phenol
72 kg/day phenol
157 kg/day DIPE
Distillation Column
70 kg/day phenol
2 kg/day DIPE
For sale or reuse
Extractor
Pretreated Wastewater
1530 kg/day
0.5% phenol
0.2% DIPE
Makeup DIPE
5 kg/day
155 kg/day DIPE
2 kg/day phenol

Figure 5-22. Process flow sheet for treatment WET stream 02.01.03 by solvent extraction with di-isopropyl ether (DIPE).

liquid (added at the bottom) rises continuously through the heavier liquid (added at the top) which is falling. By adding packing or installing perforated plates in the tower, improved contact is obtained--although costs are also increased. This type of equipment can be designed so that either the lighter or heavier phase is dispersed (i.e., droplets of light phase rising through a continuous heavy phase or droplets of heavy phase falling through a continuous light phase).

5.8.2.2 Process Details--

A simplified flow sheet for a solvent extraction process is shown in Figure 5-22. This shows a countercurrent solvent extraction process with solvent regeneration in a distillation column followed by solvent recycle. Some solvent is unavoidably lost due to solubility of the solvent in the treated wastewater; this loss is made up with fresh solvent.

The chemical nature of the waste stream will determine the feasibility of using solvent extraction since an appropriate solvent for each application must be found. An appropriate solvent is one with a high distribution coefficient for the constituent of concern (relative to water), low solubility in water (to minimize solvent losses), low cost and low heat of vaporization (to reduce solvent recovery costs). The distribution coefficient is the ratio of the concentration of solute in solvent to the concentration of solute in wastewater at equilibrium.

Of additional concern are the environmental aspects of the solvent itself, which may be hazardous or present a volatile emissions problem. Solvents typically are highly volatile organic compounds. Thus, emissions from the pretreatment operation must be closely controlled. In addition, the pretreated wastewater will be saturated with the process solvent and the emissions associated with volatilization of that solvent during storage or following land application of the pretreated wastewater must be considered. If the recovered wastes are of low economic value they may be incinerated with or without energy recovery. In such cases, appropriate controls on emissions from the incineration facility are required.

The components removed from the pretreated wastewater are recovered in concentrated form with a small fraction of residual solvent. Ideally, these materials will be reused. Where reuse is impractical (due to low economic value, low purity, or the complex nature of the recovered byproduct), incineration or ultimate disposal (e.g., landfill) of the concentrated byproduct will be necessary.

5.8.2.3 Existing Sites--

Solvent extraction is widely used in the oil refining and organic chemicals industries. In addition, waste treatment facilities employing solvent extraction are commonly associated with coke ovens (and, to a lesser extent, other iron and steel processing wastes) and pulp and paper processing.

Earhart (1976) has reported on solvent extraction processes applied to the treatment of organically contaminated wastewater produced in refinery and organic chemicals manufacturing operations. The following specific applications were cited:

1. n-Butyl acetate and isobutylene are used to remove phenol, cresol and to decrease the chemical oxygen demand (COD) by wastewater produced in crude oil refining.
2. 1-Butylene is used to decrease COD in cresylic acid manufacturing wastewater.
3. Isobutane is used to decrease COD from ethylene plant quench water.
4. The wastewater from the manufacture of ethylene dichloride is extracted with octanol to remove chloral. Octanol is sparingly soluble in this wastewater and is removed by subsequent extraction with isobutane.
5. n-Butyl acetate and isobutylene are used to remove phenol from wastewater produced in the manufacture of phenol formaldehyde resin.
6. Methyl isobutylketone is used to remove organics from hydrofiner wastewater.
7. Isobutylene is used to remove aromatics and COD from styrene manufacturing wastewater.

Based on laboratory and pilot-scale studies, Pibble (1980) reported on the use of dodecylphenol as a solvent for extraction of caprolactam from aqueous streams. The concentration of caprolactam was reduced from 600 mg/L to 30 mg/L by extraction with a 10:1 water to solvent ratio. In addition the process was also conducted on streams containing as much as 25 percent caprolactam.

Ricker and King (1980) reported on the removal of acetic acid from wastewater using ethylacetate and cyclohexane as solvents. For concentrated waste streams the value of the recovered acetic acid exceeded estimated treatment costs. Himmelstein (1974) reported on solvents with distribution coefficients of between 10 and 50 for this application.

Woods and Slezak (1973) extracted dispersed oily steel mill waste with toluene and hexane in a six-stage laboratory extraction column. By using an electrolyte to destabilize the colloidal oil, a major reduction in turbidity was observed.

Hwang (1981) compiled distribution coefficients for 89 different organic priority pollutants in approximately 20 different organic solvents. The costs for solvent extraction were found to be "considerably dependent" on the value of the recovered organics. Kiezyk and Mackay (1971) have reviewed the application of solvent extraction to wastewater treatment for phenol removal, oily water treatment, and acetic acid recovery.

5.8.2.4 General Economics--

Hwang (1981) addressed cost-effectiveness for the general case of solvent extraction treatment of aqueous wastes and found the value of recovered materials to be a primary importance. A capital cost of $2 million (1981 $) was estimated for a 400 gal/min wastewater stream that required stainless steel equipment. For a general case, Hwang estimated total costs of $11.30/1000 gallons for a stream of this flow rate. Makeup solvent costs are responsible for a large part of the operating cost; however, total costs can be offset by the value of the recovered material.

Ricker and King (1980) investigated the costs of removing acetic acid from wastewater. For a 100 gal/min stream containing 5 percent acetic acid, the installed capital cost was estimated at $1,030,000 (1978 $); operating costs were estimated at $253,000/year. This resulted in a return on investment of 244 percent/year. For a 1 percent acetic acid stream of the same volumetric flow rate, the return on investment was 30 percent/year. These costs were based on the use of mixed solvent systems of long chain akylamines.

5.8.3 Example Case

5.8.3.1 WET Stream Chosen--

Stream 02.01.03, "Phenol-Formaldehyde Solution from Plastics Production" is an aqueous stream containing 5 percent phenol and 2 percent formaldehyde. It has a flow rate of 1,600 kg/day.

5.8.3.2 Economics--

The stream chosen is relatively low in volume, although well suited chemically for solvent extract treatment. Because such low-volume waste streams do not permit economies of scale, the treatment process is expensive. However, it is possibile to treat several streams together, either after transporting them to a central facility, of by combining similar streams produced at one location. Accordingly, a rough cost estimate (±30%) has been made for treatment of a stream of equal concentration and ten times the volumetric flow rate of WET stream 02.01.03.

Installed capital cost of a solvent extraction/solvent recovery system for this stream is $210,000 (1983 $) with an annual operating cost of $40,000 and a total annualized cost of $34,217. Such a system would remove 118,181 kg of phenol per year. The unit cost is thus $0.059/kg waste stream treated.

A process flow sheet along with a mass balance for the solvent extraction treatment of WET stream 02.01.03 by extraction with di-isopropyl ether is given in Figure 5-22.

These data are simplified, as they do not consider other organic material present in the wastewater. In an actual case, a significant amount of the formaldehyde in the wastewater would also be transferred to the solvent phase. The recovered byproducts could be separated in the solvent recovery operation.

Solvent extraction is a mature technology in the chemical process industries and specific industrial wastes have been treated by solvent extraction for many years. However, use of this technique for the removal of volatile constituents from a hazardous waste stream will only follow successful laboratory and pilot plant studies to optimize solvent selection and operating conditions (solvent to wastewater ratio, number of stages, etc). Beyond this, for a wastewater stream of constant composition, all of the uncertainties are economic in nature. Typical uncertainties are the future values of the recovered constituent, and the future costs of the solvent and process energy.

5.8.4 Advantages and Disadvantages

The primary advantage of solvent extraction is that the extracted materials can be recovered for sale or reuse. The primary disadvantage is that the removed material is not destroyed and in cases where it can not be sold or reused additional costs are incurred for final disposal. This may be the case where the removed volatile material is of little economic value or where a number of components are removed from a waste stream together and are not easily separated for individual reuse. Two additional disadvantages are important. First, there is the unavoidable contamination of the pretreated wastewater with a small amount of solvent which, if it is highly volatile, may present emissions problem itself. Second, there is the potential emissions of solvent from the actual extraction and solvent regeneration operations.

5.8.5 Recommendations for Further Study

Initial laboratory studies to determine the optimal solvent must be conducted for each individual waste stream considered for pretreatment by solvent extraction. This is necessary because the presence of wastewater components, other than the components to be removed, can influence the distribution coefficients. Following laboratory selection of a solvent, pilot studies are required. These are necessary to determine mass transfer rates for sizing equipment, as well as to optimize the solvent to wastewater ratio and other operating conditions.

5.9 PHYSICAL SEPARATION

5.9.1 Introduction

Physical separation as applied to hazardous waste pretreatment involves the separation of two liquid phases or the separation of a solid phase from a liquid phase. For example, two liquid phases may be separated into an organic phase containing volatile materials and an aqueous phase containing much lower levels of dissolved organics. This may be accomplished in some cases by allowing the phases to separate in a tank and then either skimming the phase of lower density (usually the organic phase) or decanting the phase of higher density. More complex wastes, where the two phases may be dispersed or emulsified, may require the addition of chemicals to promote phase separation.

The advantages of such a separation are substantial. A large reduction in the volume of hazardous waste may be achieved, and, in some cases, both phases can be reused. In other cases, the recovered organic phase may be incinerated while the aqueous phase is suitable for land application.

In cases where a solid phase is to be separated from a liquid phase, the separation can be brought about by gravity or filtration. The physical form of the waste streams can range from dilute suspensions of fine particles in a liquid, to heavy sludges consisting primarily of solid matter suspended within a liquid phase. The compounds responsible for potential hazardous emissions may be present in either phase. In cases where the waste is composed of particles suspended in a liquid that contains dissolved hazardous compounds, the particulate matter may be removed to simplify further processing of the liquid phase (e.g., pumping, distillation, stripping, etc.).

Separation of liquids from solids can be accomplished by sedimentation (with or without flocculation or coagulation), centrifugation, flotation, filtration, or drying. Separation of two liquid phases can be accomplished by skimming or decanting (with or without further chemical treatment).

5.9.2 State of the Art

5.9.2.1 General Process Description--

5.9.2.1.1 Solid/liquid separation--Sedimentation is a process designed to remove suspended solids from liquids. Particles of greater density than the stream in which they are suspended fall to the bottom of a tank where they are removed mechanically along with some of the liquid; the treated liquid, which is relatively particle free, is allowed to overflow. The process is typically operated in a continuous mode. Equipment size is determined by observing settling velocities in a laboratory and designing a sedimentation tank with sufficient residence time for the particle to reach the bottom. This residence time is determined primarily by the difference in density between the particles and the suspending liquid, and the size of the particles (which affects drag forces).

Removal efficiencies can be improved by flocculating and coagulating small particles to produce larger particles that settle more rapidly. A wide range of chemicals are available to promote this action. Selection of the chemical to be used depends on the chemical nature of the particulate matter. The basic principle of coagulation is to alter the surface charges of the particles to make them more likely to combine. This action can be promoted by gentle agitation (flocculation) in a separate vessel where the particles bump against each other to promote interparticle adhesion.

Centrifugation accelerates the waste stream centrifugally thus causing the heavier component (usually the solid) to concentrate on the outer extreme of the centrifuge where it can be removed in a concentrated form. Rapid rotation can greatly increase the acceleration and thus shorten processing times (compared to sedimentation) at the expense of increased energy cost.

The flotation process is the reverse of sedimentation. The lighter particles rise to the top of the tank where they are skimmed or allowed to overflow. A modification of this operation, referred to as dissolved air flotation, employs air bubbles which adhere to the particles and decrease the density of the particle/bubble combination, and thus promote the transport of particles to the top of the vessel.

Filtration involves forcing of the liquid-solid mixture through a porous medium that traps the particles and allows the liquid to pass through. This can be accomplished using applied external pressure or gravity. Filter media range from fabrics to sand beds. Drying involves the separation and removal of the liquid from the liquid-solid mixture by evaporation.

5.9.2.1.2 Liquid-liquid separations--Immiscible liquids will separate under the force of gravity. Thus, a mixture of two immiscible liquids, typically an organic and an aqueous phase, may separate if stored in a tank, and the phase of lower density can be skimmed from the top. Separation may be complicated by the formation of emulsions. Various chemical treatments may be attempted in this case to separate phases and permit skimming of the lighter phase.

5.9.2.2 Applications--

Rosenberg et al. (1976) have described practices for the separation of sludges and oily liquids generated in a refinery. Leaded gasoline sludge is commonly treated by allowing organic lead to evaporate into the atmosphere and liquids to drain by gravity to a sewer. Oily wastewater is treated in A.P.I. separators to separate floating oil. Following this treatment, additional oil may be removed with dissolved-air flotation. Some sludges are subjected to centrifugation or vacuum filtration to remove liquids and thereby reduce the volume of solids to be landfilled.

O'Shaughnessy et al. (1981) described the removal of pigments from flexographic ink using chemical coagulation, followed by centrifugation and filtration; this reduces the volume of the sludge to 5 percent of the original volume. Lessells (1980) reported that evaporation of volatile material from the solids was a lower cost (both capital and operating) method of treatment for this stream. McLaughlin et al. (1980) used cationic and nonionic polymers to flocculate colloidal dirt from woolscour effluent prior to removal by dissolved-air flotation.

In the iron and steel industry, a 15 million gal/day melt shop and rolling mill wastewater stream is treated through a combination of sedimentation and oil skimming in a vessel of 1 million gallon capacity. Capital cost for this system at Republic Steel was reported as $19 million (Iron and Steel Engineer 1979). Hammann (1978) reported on polystyrene filter media used to remove 75 percent of suspended solids from rolling mill effluent. The Chrysler Corporation treats oily waste from a casting plant in a batch skimmer, after which emulsion breaker, polymer, alum, and caustic is added to float more oil which is then reskimmed (Harlow and Doran 1981).

Schematics for typical separation processes are shown in Figures 5-23 through 5-28. In a sedimentation process (Figure 5-23), the wastewater is pumped to a tank where chemicals such as polymers or alum are added. Rapid mixing is provided to dissolve these chemicals. The wastewater then flows to a flocculation tank where it is agitated gently to promote combination of the particles. Finally, the flocculated wastewater flows to the sedimentation tank where particles drop to the bottom and are pumped out as a sludge. The treated wastewater then overflows. This process is applicable to relatively dilute suspensions of particles (<1 percent). These particles

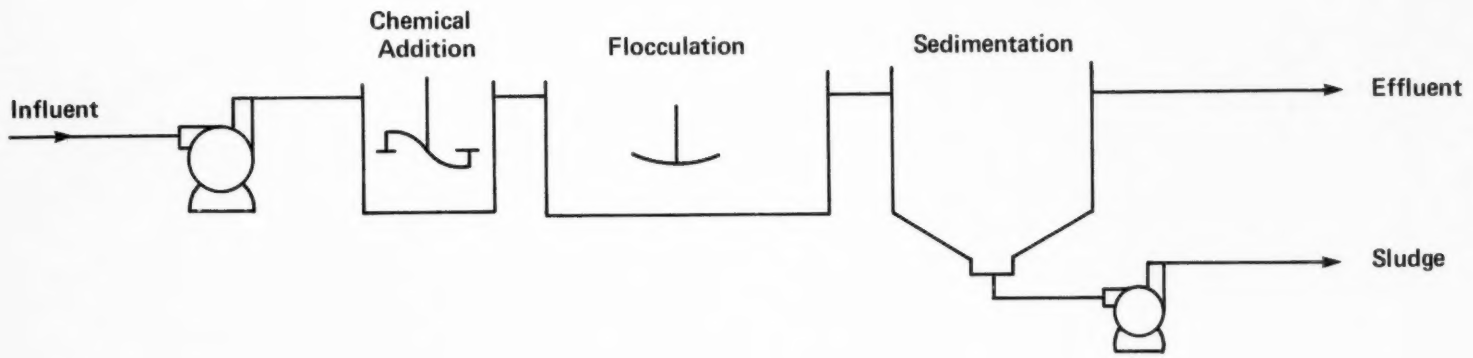

Influent
Chemical Addition
Flocculation
Sedimentation
Effluent
Sludge

Figure 5-23. Process flow sheet for sedimentation.

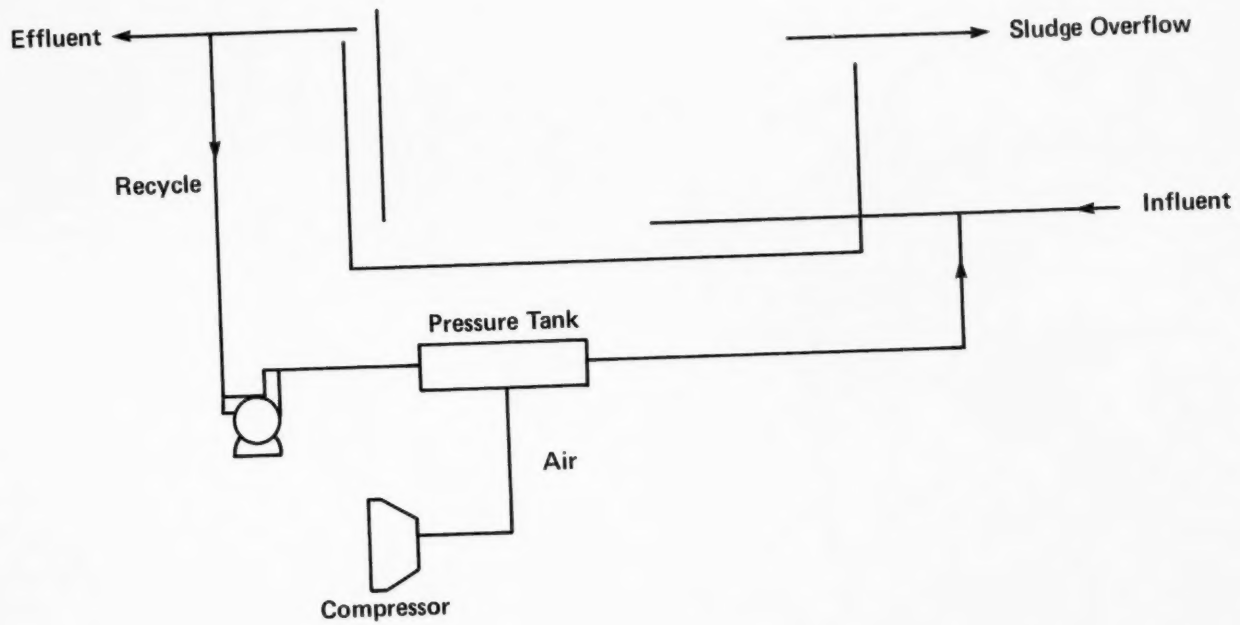

Effluent
Sludge Overflow
Recycle
Influent
Pressure Tank
Air
Compressor

Figure 5-24. Process flow sheet for dissolved air flotation.

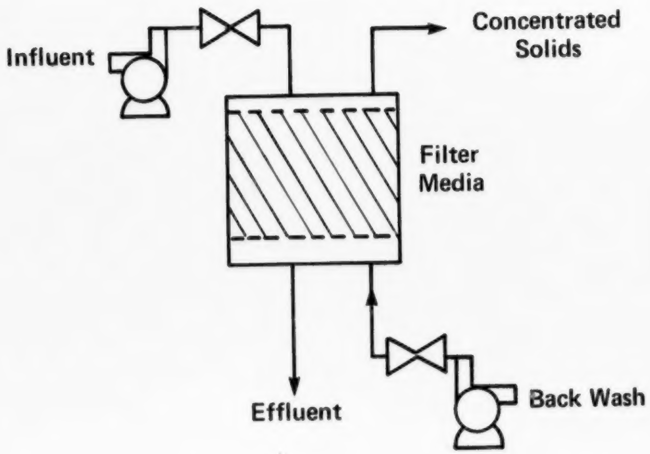

Influent
Concentrated Solids
Filter Media
Effluent
Back Wash

Figure 5-25. Process flow sheet for sand filtration.

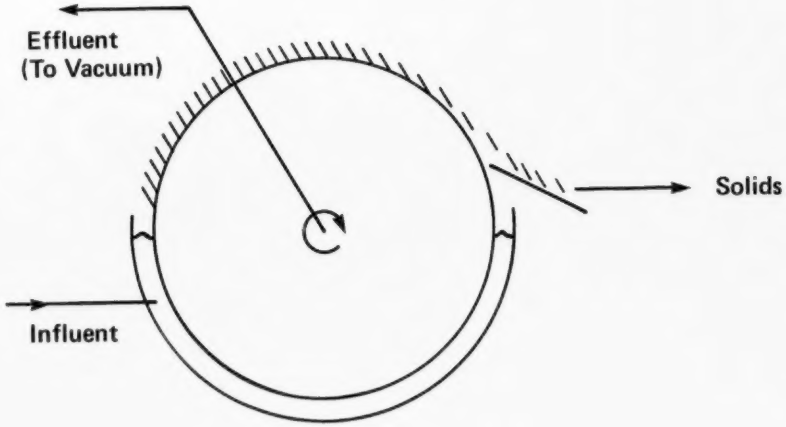

Effluent (To Vacuum)
Influent
Solids

Figure 5-26. Process flow sheet for vacuum filtration.

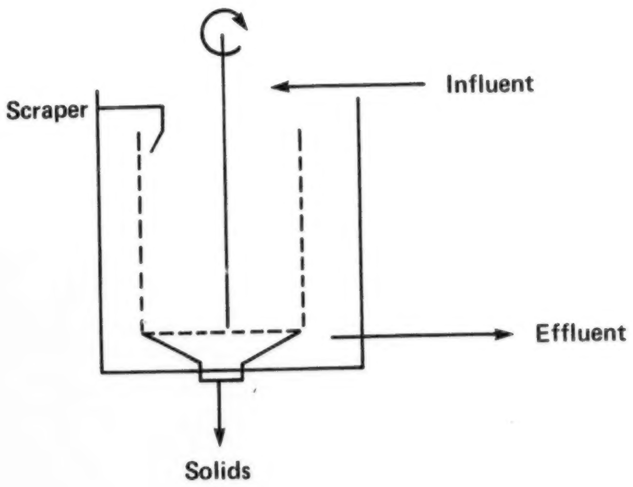

Scraper
Influent
Effluent
Solids

Figure 5-27. Process flow sheet for centrifugation.

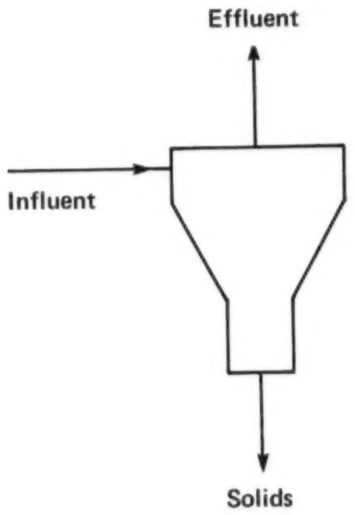

Effluent
Influent
Solids

Figure 5-28. Process flow sheet for a hydrocyclone.

are recovered in more concentrated form but the sludge is rarely more than 5 percent solids. Even though the solids are not highly concentrated, a large reduction in volume has been achieved. In the event that the solids represent the hazardous component, the smaller volume can be processed more easily. In the more common case, where the volatile material stays in the liquid phase, removal of solids simplifies additional processing such as distillation, steam stripping, solvent extraction, and carbon adsorption.

Figure 5-24 gives a schematic of a dissolved air flotation system. In this process, some of the effluent is saturated with air at elevated pressure and returned to the tank. The air is released in the form of small bubbles which attach to particles present in the effluent. The particles are brought to the surface where they overflow or are skimmed. The process is applicable to streams suitable for sedimentation, but it is also suitable for streams containing dispersed oil and grease. Unlike sedimentation, the oil droplets are removed along with the heavier particulates as a concentrated sludge. Removal efficiencies of 90+ percent can be obtained. The presence of air bubbles in the wastewater may promote stripping of volatile materials, and the extent of such emissions must be determined from pilot-scale experiments.

Filtration is commonly applied to separate solids from liquids. The simplest type of gravity filter is shown in Figure 5-25. In this process wastewater is passed through a bed of sand which retains the particles and permits clear liquid to pass through. The particles are later recovered by backwashing the filter with some of the treated effluent. This produces a concentrated suspension of particles since only a small fraction of the treated water is used for backwashing, and up to 99 percent removal can be achieved using this method.

A rotary vacuum filter is shown in Figure 5-26. In this technology a drum covered with a porous filter material is rotated through a trough of wastewater. A vacuum is applied to the inside of the drum, causing liquids to penetrate and solids to accumulate on the outside of the drum as a filter cake. These solids are scraped off as the drum rotates. This equipment is best suited to concentrated solid-liquid mixtures (>1 percent) and produces a concentrated stream of solids. The dryness of the solids is determined by the rotational speed and the applied vacuum. At slow speeds, a drier solid stream is produced as more time is available for residual moisture to be sucked through the filter.

A rotating basket centrifuge is shown in Figure 5-27. In this equipment, a solid-liquid mixture is fed to the inside of a porous rotating basket. Liquids are forced through the basket by centrigugal force and removed. Solids are scraped continuously from the inside of the basket and removed separately. The process is suitable for concentrated (>1 percent solids) suspensions and can be up to 99 percent efficient for removing solids from the liquid phase. The solids are recovered as a thick dry (<90 percent liquid) sludge.

A hydrocyclone is shown in Figure 5-28. This device also operates using centrifugal force. Wastewater containing a low concentration of particles is accelerated around the inside of a cone. The denser particles move preferentially to the wall and are eventually removed at the bottom of the device. The particle-free liquid is removed from the top.

5.9.2.3 Existing Applications--

The techniques of physical separation are in general use in the chemical processing industry and in municipal and industrial waste treatment systems. A selected list of applications is given in Table 5-29.

5.9.2.4 General Economics--

Kiang and Metry (1982) estimated that a centrifuge system with a dry solids capacity of 5.45 Mg/day would have an installed capital cost of approximately $140,000. Total capital and operating costs for centrifugation were estimated at $22-$49/Mg dry solids removed. Vacuum filtration costs were in the same range. Granular media filters (including sand filters) were estimated to cost $0.027 to $0.13/1,000 liters of wastewater treated.

5.9.3 Example Case

5.9.3.1 WET Stream 05.01.03--

Sludge from tin plating mill operations was chosen because of its high fraction of solids (estimated at 10 percent), its toxicity (high concentrations of chromium and lead), and the presence of oil and grease in the liquid phase which will require further treatment to prevent volatile emissions.

TABLE 5-29. APPLICATIONS USING PHYSICAL SEPARATION EQUIPMENT

Centrifuges	Purification of used oil Food processing Pharmaceuticals Dewatering of municipal sewage sludge Pigment wastewaters
Vacuum filtration	Purification of oil Mineral processing Pulp Pigment Sewage sludge
Sand filters	Potable water
Sedimentation	Iron and steel wastes Mineral processing Food processing Sewage Textile wastes Metal finishing
Dissolved air flotation	Sewage Textiles wastewater Iron and steel wastewater

5.9.3.2 Process Details--

A process flow sheet for the removal of solids from this stream is shown in Figure 5-29, and a mass balance for this process is given in Table 5-30. The process is straightforward, but it is only a separation step with no destruction of either the toxic metals or the potentially volatile organics. A concentrated volume of sludge material is produced to simplify landfilling, and the liquid is amenable to pumping and further processing as needed. The possibility also exists to upgrade the liquid for reuse.

The major design variable is the sizing of the centrifuge which is dependent on the volumetric flow rate of the wastewater and the difference in density between the solids and liquids.

5.9.3.3 Economics--

A 4-inch tubular bowl centrifuge has an approximate purchase price of $25,000 (Perry and Chilton 1973; adjusted to 1983 $). Installation including auxilliaries and control equipment is estimated to be 250 percent of the purchase price, yielding a total capital cost of approximately $88,000. Based on the ratio of capital to operating costs given by Kiang and Metry (1982) annual operating costs would be approximately $10,000.

As an intermediate step (which simplifys further processing) to reduce volatile emissions, the cost effectiveness of centrifugation can only be assessed in terms of downstream processing. If an 80 percent reduction in volume for land treatment could be effected, centrifugation of this waste might save approximately $32,000 in disposal-related costs.

5.9.4 Advantages and Disadvantages

The main advantages of physical separation for waste pretreatment are reduced volume (due to concentration of the hazardous material in one of the phases) and the simplification of downstream processing due to removal of solids. Neither phase is destroyed and recovery and reuse is possible. In cases where oily wastes are concentrated, the recovered material may be suitable for incineration with energy recovery. If incineration with auxilliary fuel is required, the concentrated stream may be more readily incinerated at lower cost.

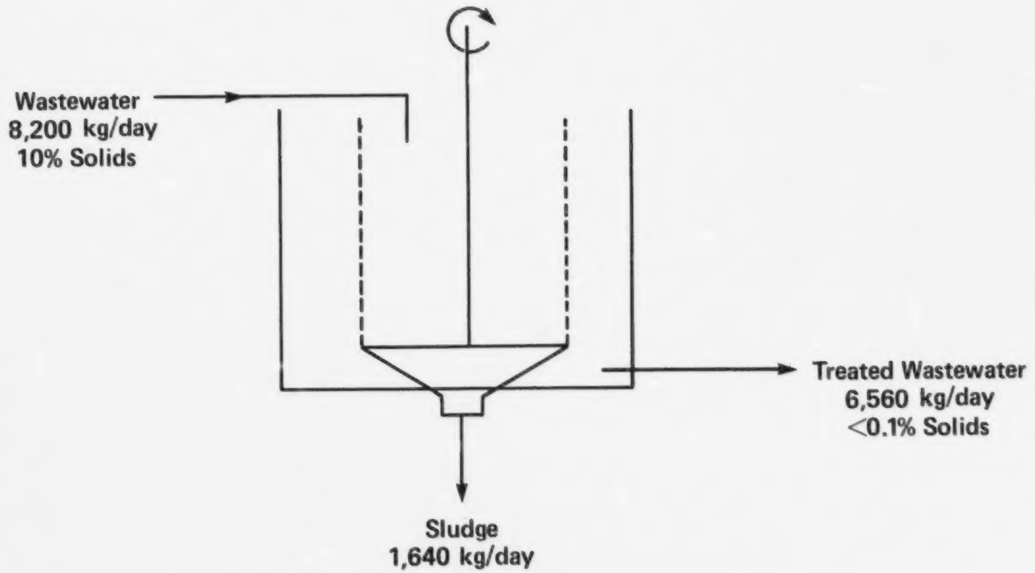

Wastewater
8,200 kg/day
10% Solids
Treated Wastewater
6,560 kg/day
<0.1% Solids
Sludge
1,640 kg/day

Figure 5-29. Process flow sheet for pretreatment by centrifugation of WET stream 05.01.03 (sludge from tin plating).

TABLE 5-30. MASS BALANCE FOR TREATMENT OF WET STREAM 05.01.03 BY CENTRIGUATION

		kg/day
IN:	Wastewater	
	Solids	820
	Liquid	7,380
		8,200
OUT:	Treated wastewater	
	Solids	≤7
	Liquid	6,560
		6,560
	Sludge	
	Solids	820
	Liquid	820
		1,640

The disadvantage of these processes is that the hazardous material is only concentrated and not destroyed, so that further processing of both streams is required. In some cases, emissions from separation processes will require control. Sedimentation tanks are commonly designed with large open surface areas and emissions of volatiles may occur during processing. Dissolved air flotation systems may promote volatilization due to stripping of volatiles components from the liquid by air bubbles.

5.9.5 Recommendations for Further Study

Individual waste streams must be tested to optimize residence times and equipment size. Most of the separation techniques discussed are standard practice in various industries. The adaptation of these techniques to different waste streams is also one of the responsiblities of equipment vendors.

SECTION 6

PRETREATMENT-WASTE STREAM APPLICABILITY

To provide an indication of the applicability of the pretreatment techniques discussed in Section 5 for removal of volatile constituents (i.e., compound with a significant vapor pressure at ambient conditions) from all of the WET Model streams*, a matrix has been developed and is shown in Table 6-1. It should be noted that the WET Model stream information herein is based on preliminary data. The data on stream composition and generation rate is likely to change as the model is updated. This matrix has been constructed by assigning a letter grade to every combination of pretreatment technique and waste stream constituent. The grades and the criteria by which a grade is assigned are:

A - Demonstrated at a commercial scale for volatile removal from a similar hazardous waste stream.

B - Directly applicable to volatile removal. A clear candidate for technology transfer (in use on some process streams at a scale appropriate to hazardous waste pretreatment).

C - Probably applicable. May require a slight process design change (for example, a preconditioning step upstream of the process) or modest scale-up.

D - May be applicable. Not demonstrated on a commercial scale either for general process streams or for hazardous waste streams. Proof of concept needed for application to volatile removal from hazardous waste streams.

E - Not applicable. Not conceptually valid for volatile removal from hazardous waste streams.

Note that in Table 6-1, a grade has been assigned to each volatile component in each waste stream. This was done since it was deemed that a distinction between the applicability of a technique to a stream versus the applicability of a technique to a component in a stream was needed. Thus,

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*Waste streams are described in Appendix C.

TABLE 6-1. WASTE STREAM-PRETREATMENT APPLICABILITY*

WET stream number	Constituent	Total amount gener-ated, kg/day	Steam strip-ping	Chem-ical oxida-tion	Carbon adsorp-tion	Resin adsorp-tion	Evapor-ation/ adsorp-tion	Air strip-ping/ adsorp-tion	Biolog-ical treat-ment	Ozon-ation/ radiol-ysis	Batch continuous distil-lation	Wet oxida-tion	Solvent extrac-tion	Physi-cal separa-tion
01.01.02	Mercury	17	E	E	C	C	E	E	E	E	E	E	E	C
01.01.03	Mercury	404	E	E	C	C	E	E	E	E	E	E	E	C
01.01.12	Mercury	1,228	E	E	C	C	E	E	E	E	E	E	E	C
01.03.01	Cyanide	1,468	E	A	B	B	D	D	E	C	E	B	E	E
01.03.01	Phenol	198	E	B	B	B	D	D	C	C	E	B	C	E
01.03.02	Cyanide	950	E	B	B	B	D	D	E	C	E	B	E	E
02.01.01	Chlorophenol 2,	<1	B	D	B	B	D	D	E	C	C	D	D	E
02.01.01	Pentachlorophenol	35	B	D	B	B	D	D	E	C	E	D	D	E
01.01.02	Phenol	8,160	B	B	B	B	D	B	C	D	E	B	B	E
02.01.03	Formaldehyde	26,112	B	D	A	A	C	C	C	D	E	D	C	E
02.01.03	Phenol	65,280	B	B	A	A	C	C	C	D	E	B	B	E
02.02.01	Acetic acid	16,425	C	D	A	B	B	A	B	D	E	D	D	E
02.02.01	Acetyl chloride	6,570	C	E	A	B	B	A	E	D	E	D	D	E
02.02.01	Chloral	3,285	C	E	A	B	B	A	E	D	E	D	B	E
02.02.01	Chloroform	3,285	C	E	A	B	B	A	E	D	E	D	D	E
02.02.01	Formaldehyde	3,285	C	D	A	B	B	A	C	D	E	D	D	E
02.02.02	Acetonitrile	52,290	D	D	A	B	B	B	D	C	E	D	D	E
02.02.02	Acrylonitrile	3,486	D	D	A	B	B	B	D	C	E	D	D	E
02.02.02	Cyanide	26,145	D	B	A	B	B	B	E	C	E	B	E	E
02.02.03	Carbon tetrachloride	1	B	D	A	B	C	B	E	C	E	D	D	E
02.02.03	Chloroform	1	C	D	A	B	C	B	E	C	E	D	D	E
02.02.04	Aniline	11	C	D	A	B	C	B	C	C	E	D	D	E
02.02.04	Benzene	548	B	D	A	B	C	B	D	C	E	D	C	E
02.02.04	Nitrobenzene	384	C	D	A	B	C	B	C	C	E	D	C	E
02.02.05	Benzene	3	B	D	A	B	C	B	D	C	E	D	B	E
02.02.05	Chlorobenzene	<1	B	E	A	B	C	B	E	C	E	D	D	E
02.02.05	Dichlorobenzene (1,2)	<1	B	E	A	B	C	B	E	C	E	D	D	E
02.02.05	Dichlorobenzene (1,4)	<1	B	E	A	B	C	B	E	C	E	D	D	E
02.02.06	Paraldehyde	219	C	D	B	C	D	D	D	E	B	D	D	E
02.02.06	Picoline (2-)	18	C	D	B	C	D	D	D	E	C	D	D	E
02.02.06	Pyridine	18	C	D	A	A	D	D	D	E	B	D	D	E
02.02.07	Toluene	290	B	D	A	B	D	B	D	D	E	D	B	E
02.02.08	Benzene	41,550	B	D	A	C	D	A	D	E	E	D	B	E
02.02.08	Maleic anhydride	249	C	D	A	C	B	A	C	E	E	D	D	E
02.02.09	Carbon tecrachloride	472	B	E	A	C	B	B	E	E	B	D	D	E
02.02.09	Chlorothane	8,968	B	E	C	D	B	B	E	E	B	D	D	E
02.02.09	Chloroform	472	B	E	C	D	B	B	E	E	B	D	D	E
02.02.09	Dichloroethane (1,2)	103,368	B	E	C	D	B	B	E	E	B	D	D	E
02.02.09	Methyl chloride	944	B	E	C	D	B	B	E	E	B	D	D	E
02.02.09	Methyl chloride	9,912	B	E	C	D	B	B	E	E	B	D	D	E
02.02.09	Vinyl chloride	11,800	B	E	C	D	B	B	E	E	B	D	D	E
02.02.10	Maleic anhydride	8,250	C	D	A	A	E	D	C	D	E	D	D	E
02.02.10	Phthalic anhydride	83	C	D	A	A	E	D	C	D	E	D	D	E
02.02.11	Aniline	25,600	C	D	A	A	E	C	C	D	E	D	D	E
02.02.12	Acetaldehyde	6,636	C	D	D	E	C	B	C	E	B	D	D	E
02.02.13	Benzene	<1	B	D	A	A	C	A	D	C	E	D	B	E
02.02.13	Phenol	<1	B	B	A	A	C	A	D	C	E	B	B	E
02.02.13	Toluene	<1	B	D	A	A	C	A	D	C	E	D	B	E
02.02.14	Benzene	74,550	B	D	A	A	D	C	D	C	E	D	B	E
02.02.14	Phenol	44,730	B	B	A	A	D	C	C	C	E	B	B	E
02.02.14	Toluene	59,640	B	D	A	A	D	A	D	C	E	D	B	E
02.02.15	Methyl methacrylate	11,484	C	D	B	C	C	C	C	C	B	D	D	E
02.02.16	Phenol	84,000	B	B	A	A	E	D	C	D	E	B	B	E

(continued)

TABLE 6-1 (continued)

WET stream number	Constituent	Total amount generated, kg/day	Steam stripping	Chemical oxidation	Carbon adsorption	Resin adsorption	Evaporation/adsorption	Air stripping/adsorption	Biological treatment	Ozonation/radiolysis	Batch continuous distillation	Wet oxidation	Solvent extraction	Physical separation
02.02.17	Ethylene oxide	43,650	D	D	A	C	B	D	D	C	E	D	D	E
02.02.18	Formaldehyde	5,250	C	D	B	C	B	C	C	D	E	D	D	E
02.02.19	Phenol	4,225	A	B	A	A	E	D	C	D	E	B	B	E
02.02.20	Carbon tetrachloride	1,560	A	E	A	A	C	A	E	E	E	D	D	E
02.02.21	Phenol	360	A	B	B	B	E	D	C	C	B	B	D	E
02.02.22	Methyl ethyl ketone	1,152	A	D	B	C	C	C	C	D	E	D	D	E
02.02.23	Methyl ethyl ketone	148	A	D	B	C	C	C	C	E	B	D	D	E
02.03.01	Toxaphene	138	D	E	C	D	E	E	E	E	E	D	D	E
02.03.90	Parathion	40,827	E	E	C	D	E	E	E	E	E	D	D	E
02.03.91	Chlordane	40,827	E	E	B	C	E	E	D	E	E	D	D	E
02.04.01	Acenaphthene	31	D	D	B	C	E	E	D	E	E	D	B	E
02.04.01	Chrysene	10	D	D	B	C	E	E	D	E	E	D	B	E
02.04.01	Fluorene	29	D	D	B	C	E	E	D	E	E	D	B	E
03.01.04	Tetrachloroethene	48,960	D	E	C	D	E	E	E	E	B	D	D	E
03.01.05	Dichloromethane	2,278	D	E	E	E	A	D	E	E	D	D	D	E
03.01.05	Hexane	16,600	B	D	E	E	A	D	D	E	B	D	D	E
03.01.05	Tetrachloroethane	4,014	D	E	E	E	A	D	E	E	B	D	D	E
03.01.05	Toluene	1,031	D	D	E	E	A	D	D	E	B	D	D	E
03.01.05	Trichloroethane (1,1)	12,043	D	E	E	E	A	D	E	E	B	D	D	E
03.01.05	Trichloroethylene	11,392	D	E	D	E	A	D	E	E	D	D	D	E
03.01.06	Trichloroethane (1,1)	8,680	E	E	D	E	A	D	E	E	B	D	D	E
03.01.08	Trichloroethylene	8,680	E	E	D	E	B	D	E	E	B	D	D	E
03.01.90	Toluene	32,880	D	D	E	E	A	D	D	E	B	D	D	E
03.02.01	Trichloroethylene	63	E	E	E	E	B	D	E	E	B	D	D	E
03.02.90	Toluene	8,220	D	D	E	E	B	D	D	E	B	D	D	E
03.04.01	Benzal chloride	22,448	E	E	E	E	C	E	E	E	B	D	D	E
03.04.01	Hexachlorobenzene	92	E	E	E	E	C	E	E	E	B	D	D	E
03.04.01	Toluene	69	E	D	E	E	C	E	D	E	B	D	D	E
03.04.01	Trichlorobenzene	92	E	E	E	E	C	E	E	E	B	D	D	E
03.04.02	Chloroethers	2,436	E	E	E	E	A	E	E	E	B	D	D	E
03.04.02	Dichloropropanol	1,740	E	E	E	E	A	E	E	E	B	D	D	E
03.04.02	Epichlorohydrin	348	E	E	E	E	A	E	E	E	B	D	D	E
03.04.02	Trichloropropane	12,180	E	E	E	E	A	E	E	E	B	D	D	E
03.04.03	Dichloroethane (1,2)	8,910	E	E	E	E	A	D	E	E	B	D	D	E
03.04.03	Hexachlorobenzene	17,415	E	E	E	E	A	D	E	E	B	D	D	E
03.04.03	Hexachlorobutadiene	17,415	E	E	E	E	A	D	E	E	B	D	D	E
03.04.03	Trichloroethylene	25,920	B	E	E	E	A	D	E	E	B	D	D	E
03.04.04	Ethylene dichloride	45,176	B	E	E	E	A	D	E	E	B	D	D	E
03.04.04	Tetrachloroethane	53,071	B	E	E	E	A	D	E	E	B	D	D	E
03.04.04	Trichloroethane	53,071	B	E	E	E	A	D	E	E	B	D	D	E
03.04.05	Dichloroethane	34,848	B	E	E	E	A	D	E	E	B	D	D	E
03.04.05	Tetrachloroethane	30,384	B	E	E	E	A	D	E	E	B	D	D	E
03.04.05	Trichloroethane	39,168	B	E	E	E	A	D	E	E	B	D	D	E
03.04.05	Vinyl chloride	288	E	E	E	E	A	D	E	E	B	D	D	E
03.04.06	Maleic anhydride	1,980	E	D	E	E	C	E	C	E	B	D	D	E
03.04.06	Phthalic anhydride	220	E	D	E	E	C	E	C	E	B	D	D	E
03.04.07	Maleic anhydride	935	E	D	E	E	C	E	C	E	B	D	D	E
03.04.07	Phthalic anhydride	4,565	E	D	E	E	C	E	C	E	B	D	D	E
03.04.08	Cyclohexane	3,180	B	D	E	E	A	E	D	E	B	D	D	E
03.04.09	Dinitrobenzene-M	1,306	E	D	E	E	C	E	C	E	B	D	D	E
03.04.09	Dinitrotoluene (2,4)	781	E	D	E	E	C	E	D	E	C	D	D	E
03.04.09	Nitrobenzene	1,696	E	D	E	E	C	E	C	E	B	D	D	E
03.04.09	Nitrophenol (4)	130	E	D	E	E	C	E	D	E	C	D	D	E

(continued)

TABLE 6-1 (continued)

WET stream number	Constituent	Total amount generated, kg/day	Steam stripping	Chemical oxidation	Carbon adsorption	Resin adsorption	Evaporation/ adsorption	Air stripping/ adsorption	Biological treatment	Ozonation/ radiolysis	Batch continuous distillation	Wet oxidation	Solvent extraction	Physical separation
03.04.10	Carbon tetrachloride	2,500	E	E	E	E	A	D	E	E	B	D	D	E
03.04.10	Trichloroethylene	200	E	E	E	E	A	D	E	E	C	D	D	E
03.04.11	Hexachlorobenzene	26,600	E	E	E	E	C	D	E	E	B	D	D	E
03.04.11	Hexachlorobutadiene	44,954	E	E	E	E	C	D	E	E	B	D	D	E
03.04.11	Tetrachloroethane	38,969	E	E	E	E	C	D	E	E	B	D	D	E
03.04.12	Hexachlorobenzene	1,260	E	E	E	E	D	D	E	E	B	D	D	E
03.04.13	Benzo(a)anthracene	344	E	D	E	E	D	E	D	E	B	D	D	E
03.04.13	Benzo(a)pyrene	344	E	D	E	E	D	E	D	E	B	D	D	E
03.04.13	Chrysene	344	E	D	E	E	D	E	D	E	B	D	D	E
03.04.13	Phenol	3,100	E	B	E	E	D	E	C	E	B	B	D	E
03.04.14	Acetaldehyde	11,664	D	D	E	E	A	D	C	E	B	D	D	E
03.04.14	Acetyl chloride	7,848	D	E	E	E	A	D	E	E	B	D	D	E
03.04.14	Chloral	5,256	C	E	E	E	A	D	E	E	B	D	D	E
03.04.14	Chloroacetaldehyde	8,568	C	E	E	E	A	D	E	E	B	D	D	E
03.04.14	Chloroform	1,440	C	E	E	E	A	D	E	E	B	D	D	E
03.04.14	Formaldehyde	1,440	C	D	E	E	A	D	C	E	B	D	D	E
03.04.15	Aniline	4,490	E	D	E	E	C	E	C	E	B	D	D	E
03.04.15	Benzene	287	E	D	E	E	C	E	D	E	B	D	D	E
03.04.15	Diphenylamine	5	E	B	E	E	C	E	D	E	B	D	D	E
03.04.15	Nitrobenzene	109	E	D	E	E	C	E	C	E	B	D	D	E
03.04.15	Phenylenediamine	15	E	B	E	E	C	E	D	E	B	D	D	E
03.04.16	Dichloroethane (1,2)	612	E	E	E	E	A	D	E	E	B	D	D	E
03.04.16	Trichloroethane (1,1)	2,988	E	E	E	E	A	D	E	E	B	D	D	E
03.04.17	Maleich anhydride	1,181	E	D	E	E	C	E	C	E	B	D	D	E
03.04.18	Cyclohexanol	4,897	E	D	E	E	C	E	D	E	B	D	D	E
03.04.18	Phenol	1,340	D	B	E	E	C	E	C	E	B	B	D	E
03.04.19	Benzene	3,473	E	D	E	E	A	E	D	E	B	D	D	E
03.04.19	Cyclohexane	3,473	E	D	E	E	A	E	D	E	B	D	D	E
03.04.20	Carbon tetrachloride	4,760	E	E	E	E	A	D	E	E	B	D	D	E
03.04.20	Toluene	23,800	E	D	E	E	A	D	D	E	B	D	D	E
03.04.20	Xylene	16,660	E	D	E	E	A	D	D	E	B	D	D	E
03.04.21	Benzene	12,720	E	D	E	E	A	D	D	E	B	D	D	E
03.04.21	Toluene	6,360	E	D	E	E	A	D	D	E	B	D	D	E
03.04.21	Xylene	6,360	E	D	E	E	A	D	D	E	B	D	D	E
03.04.22	Acetone	8,316	E	D	E	E	A	E	C	E	B	D	D	E
03.04.22	Methanol	22,176	E	D	E	E	A	E	B	E	B	D	D	E
03.04.22	Methyl acetate	241,164	E	D	E	E	A	E	C	E	B	D	D	E
03.04.22	Methyl ethyl ketone	2,578	E	D	E	E	A	E	C	E	B	D	D	E
03.04.23	Dichloropropene	11,925	E	E	E	E	A	E	E	E	B	D	D	E
03.04.24	Butanol(s)	22,320	E	D	E	E	A	E	C	E	B	D	D	E
03.04.24	Butyl ether(s)	14,880	E	D	E	E	A	E	D	E	B	D	D	E
03.04.24	Hydrocarbons (C5+)	16,120	E	D	E	E	A	E	D	E	B	D	D	E
03.04.24	Methyl ethyl ketone	5,580	E	D	E	E	A	E	C	E	B	D	D	E
03.04.26	Acetaldehyde	3,171	E	D	E	E	A	D	C	E	C	D	D	E
03.04.26	Acrolein	440	E	D	E	E	A	D	D	E	B	D	D	E
03.04.27	Ethanol	3,720	B	D	E	E	A	D	B	E	C	D	D	E
03.04.27	Ethyl acetate	744	D	D	E	E	A	D	C	E	B	D	D	E
03.04.27	Formaldehyde	248	D	D	E	E	A	D	C	E	B	D	D	E
03.04.27	Methanol	3,224	D	D	E	E	A	D	B	E	B	D	D	E
03.04.28	Acrolein	912	D	D	E	E	A	D	D	E	C	D	D	E
03.04.28	Dichloroethane (1,1)	91	D	E	E	E	A	D	E	E	B	D	D	E
03.04.29	Chlorophenol	176	E	E	E	E	C	D	E	E	B	D	D	E
03.04.30	Acrolein	1	E	D	E	E	B	D	D	D	C	D	D	E

(continued)

TABLE 6-1 (continued)

WET stream number	Constituent	Total amount gener- ated, kg/day	Steam strip- ping	Chem- ical oxida- tion	Carbon adsorp- tion	Resin adsorp- tion	Evapor- ation/ adsorp- tion	Air strip- ping/ adsorp- tion	Biolog- ical treat- ment	Ozon- ation/ radiol- ysis	Batch continuous distil- lation	Wet oxida- tion	Solvent extrac- tion	Physi- cal separa- tion
03.04.30	Allyl alcohol	33	E	D	E	E	B	D	B	D	B	D	D	E
03.04.30	Methyl ethyl ketone	1	E	D	E	E	B	D	C	D	B	D	D	E
03.04.31	Benzotrichloride	162	E	E	E	E	B	E	E	E	C	D	D	E
03.04.31	Hexachlorobenzene	11	E	E	E	E	B	E	E	E	B	D	D	E
03.04.31	Toluene	5	B	D	E	E	B	E	D	E	B	D	D	E
03.04.31	Trichlorobenzene	11	E	D	E	E	B	E	E	E	B	D	D	E
03.04.32	Dimethyl alkylamine	55	E	B	E	E	C	E	D	E	B	D	D	E
03.04.32	Toxaphene	11	E	E	E	E	C	E	E	E	B	D	D	E
03.05.01	Hexachlorobenzene	160	E	E	E	E	C	D	E	E	B	D	D	E
03.05.01	Hexachlorobutadiene	160	E	E	E	E	C	D	E	E	C	D	D	C
03.05.01	Hexachloroethane	800	E	E	E	E	C	D	E	E	B	D	D	C
03.05.01	Tetrachloroethane	800	E	E	E	E	C	D	E	E	B	D	D	C
03.05.02	Phthalic anhydride	979	E	D	E	E	D	D	C	E	E	D	D	C
03.05.03	Tetrachloroethane	49,572	E	E	E	E	C	D	E	E	E	D	D	C
03.05.04	Dichloroethane (1,2)	1,470	E	E	E	E	B	D	E	E	E	D	D	C
03.05.04	Hexachloroethane	1,232	E	E	E	E	B	D	E	E	B	D	D	C
03.05.04	Tetrachloroethane	1,232	E	E	E	E	B	D	E	E	B	D	D	C
03.05.04	Trichloroethane	4,770	E	E	E	E	B	D	E	E	E	D	D	C
03.05.05	Toluene diamine	<1	E	B	E	E	D	E	D	D	E	D	D	C
03.05.05	Toluene diisocyanate	3	E	B	E	E	D	E	E	D	E	D	D	C
03.05.06	Naphthoquinone-1,4	2,507	E	D	E	E	D	E	D	E	E	D	D	C
03.05.06	Phthalic anhydride	2,507	E	D	E	E	D	E	C	E	E	D	D	C
03.05.07	Dichloropropanols	6,696	E	E	E	E	C	D	E	E	E	D	D	C
03.05.07	Trichloropropane	3,224	E	E	E	E	C	D	E	E	B	D	D	C
03.05.08	Pentachlorlethane	22	E	E	E	E	C	D	E	E	B	D	D	C
03.05.08	Tetrachloroethane	506	E	E	E	E	C	D	E	E	D	D	D	C
03.05.08	Trichloroethane	635	E	E	E	E	C	D	E	E	D	D	D	C
03.05.09	Dialkylbenzene	40,425	E	D	E	E	D	D	D	E	C	D	D	C
03.05.09	Naphthalene	24,500	E	D	E	E	D	D	D	E	E	D	D	C
03.06.01	Carbon tetrachloride	102	E	E	E	E	A	A	E	E	B	D	D	D
03.06.01	Chloroform	688	E	E	E	E	C	A	E	E	B	D	D	D
03.06.02	Benzene	216	B	D	E	E	C	D	D	E	B	D	D	D
03.06.02	Naphthalene	16,200	E	D	E	E	C	D	D	E	E	D	D	D
03.06.02	Phenol	184	B	B	E	E	C	D	C	E	E	B	D	D
03.06.02	Toluene	216	E	D	E	E	C	D	D	E	E	D	D	D
03.06.03	PCB-1254	6,163	E	E	E	E	A	E	E	E	E	D	D	D
03.06.03	Trichlorobenzene	6,163	E	E	E	E	A	E	E	E	B	D	D	D
04.02.01	Benzo(a)pyrene	1,890	E	D	E	E	C	E	D	D	B	D	D	C
04.02.02	Benzo(a)pyrene	876	E	D	E	E	C	E	D	D	C	D	D	C

* Based on Preliminary, 1983 version of WET Model data base (U.S. EPA 1983b). Waste stream names are provided in Appendix C. Table includes both hazardous and potentially hazardous waste streams.

for example, the reader can see that stream 01.03.01 contains both cyanide and phenol. Chemical oxidation for the removal of cyanide from this stream is "demonstrated" (i.e., is assigned an "A") whereas chemical oxidation for the removal of phenol from this same stream is "directly applicable" (i.e., is assigned a "B").

One should also note that the pretreatment category discussed under the general subject of adsorption (Section 5.3) has been divided for the purposes of this matrix as follows:

- Carbon adsorption
- Resin adsorption
- Air stripping/adsorption
- Evaporation/adsorption

This was done for several reasons. First, adsorption is an extremely general term, even in the context of this report, and some further definition of this pretreatment technique was needed. Second, adsorption is one of the more generally applicable pretreatment techniques and thus further definition allows the reader to ascertain more specifically what type of adsorption pretreatment is best for removal of certain volatile constituents on certain streams.

The applicability rating presented in Table 6-1 was not generated by using rigorous quantitative assessment of pretreatment technique-waste steam compatibility. Such attempts encountered numerous difficulties, some of which are enumerated below:

- A lack of information regarding the bulk characteristics, i.e., physical and chemical properties, of the waste streams.
- The uncertainty associated with the available quantitative data, e.g., stream composition and bulk property data.

After several attempts at defining more rigorous criteria for assessing compatibility, it was judged that such an approach would not be possible without more detailed data on the individual waste streams. It was therefore decided to use engineering judgment, albeit subjective in many cases, in assessing the applicability of the selected pretreatment techniques to

WET Model waste streams. Regardless of the limitations, however, Table 6-1 does serve as a rough guide to establish what pretreatment techniques may be applicable to volatile removal from specific WET Model hazardous waste streams.

Although no comprehensive interpretation of the information in Table 6-1 has been attempted (due primarily to the limitations discussed above), several general conclusions can be drawn:

- Carbon adsorption is one of the most generally applicable techniques for volatile removal. When coupled with air stripping or evaporation, a great many of the WET model streams can be pretreated using this technique.
- Other techniques that are widely applicable include steam stripping, distillation, and biological treatment.
- The remaining techniques generally require further study and development before they can be considered either demonstrated or directly applicable to hazardous waste pretreatment.

One should not assume that the above judgments apply universally to all hazardous waste streams. First, the information in the WET Model, which is the basis of Table 6-1, contains only limited information about the waste streams that are listed. Second, there may be important waste streams that the WET Model does not list due to the method in which the data were obtained. However, based on the information and analysis herein, the above conclusions can be drawn. Further definition of the most applicable pretreatment techniques is clearly an area for further study.

For a detailed discussion on the limitations of the WET Model, see Section 3.

SECTION 7

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APPENDIX A

PROCESS ECONOMICS

This section describes the underlying assumptions behind the process costs and cost-effectiveness calculations for the pretreatment techniques. The cost factors for each example pretreatment process in Section 5 are presented in more detail in this chapter.

The cost of a process depends on many factors, including the volatile removal efficiency, the scale of the process, and the process design. In this report, the cost estimates for waste pretreatment do not reflect cost optimization of the design. In addition, there was no analysis of cost effectiveness as a function of the volatile removal efficiency. However, insofar as the hazardous waste streams are typical of the application the pretreatment technique, the volatile removal efficiency (kg volatile removed/kg volatile in the stream), unit cost ($/kg stream treated), and cost effectiveness ($/kg of volatile removed) are typical of what may be expected if the pretreatment technique were used on other streams of a similar nature. The cost assumptions and elements are presented in Tables A-1 through A-12 for each pretreatment technique. The cost effectiveness is expected to be much more sensitive to the volatile concentrations in the waste stream than is the unit cost because the volatile concentration typically varies over several orders of magnitude while the mass of stream treated typically varies over about one order of magnitude.

Table A-13 summarizes the removal efficiency, unit cost, and cost effectiveness of the various pretreatment techniques examined in this report. The wide range of unit cost and cost effectiveness indicates that no universal judgment can be made about the cost of hazardous waste pretreatment without a clear understanding of the chemical and physical nature of the waste stream and the process by which the volatile is to be removed. The limitations of the cost information in Table A-13 (exclusive of the fact that it is developed for only one "typical" waste stream) include:

- The removal efficiency has been arbitrarily selected, albeit using sound engineering judgment, as a rough estimate of what might be economically optimum. With few exceptions, all of the pretreatment techniques could be designed and operated for very high volatile removal efficiencies if cost were of no consequence.

- The unit cost should be regarded as an order-of-magnitude estimated at ± 50 percent, in absolute terms. However, comparison between pretreatment techniques, i.e., relative cost, may be more accurate. The reader should refer to the appropriate part of Section 5 to determine exactly what equipment is included in the cost estimate. In some cases, conditioning of a particular hazardous waste stream may be required although this is not included in the unit cost.

- The cost effectiveness calculations are based on the assumed removal efficiency and the unit cost and are thus subject to the same limitations.

- The examples are developed for the pretreatment of hazardous waste streams to remove volatiles, not to remove or destroy all hazardous components in the stream. Thus the stream may still contain hazardous components after pretreatment. Conversely, the removal of some nonvolatile constituents is inherent in some of the pretreatment techniques listed. For example, chemical oxidation will convert any readily oxidizable organic constituent whether it is volatile or not.

- The information in Table A-13 is based, in most cases, on an estimated "average" throughput (kg/day) from the WET Model. Thus, economies of scale are not considered. Another important implication, besides cost, of a different scale of equipment (i.e., different throughput) is that fundamentally new process equipment or flow configurations may be required, usually for economic reasons.

- In many examples it is assumed that the recovered product can be sold for a recovery credit. This credit often significantly reduces treatment costs. There may be waste treatment situations where no market exists for the recovered product and instead additional byproduct disposal costs will be incurred

The reader is referred to Section 5 for a discussion of each of the example processes. In addition, Berkowitz et al. (1978) is recommended for further discussion of relevant unit operations for the treatment of hazardous wastes.

TABLE A-1. ANNUALIZED COST ESTIMATES FOR THE PRETREATMENT OF WASTE STREAM 02.02.14 BY CARBON ADSORPTION

COST ELEMENT	ALL COSTS IN 1983 DOLLARS
INFLUENT PUMP STATION	21219
CARBON COLUMNS (2 pulsed bed contactors)	181000
CARBON REGENERATION SYSTEM	1925000
CARBON INVENTORY	128000
FIELD COST	2250000
TOTAL INSTALLED COST	3180000
ANNUALIZED COSTS	
MAINTENANCE (5%)	159000
FUEL, STEAM, AND WATER	903000
ELECTRICITY	41200
CARBON MAKEUP	704700
TAXES, INSURANCE, ADMINISTRATION (4%)	127200
OPERATING LABOR	540000
PRODUCT RECOVERY CREDIT	0
BYPRODUCT DISPOSAL COST	0
ANNUAL OPERATING COST	2475100
CAPITAL RECOVERY (16.3%)	518340
TOTAL ANNUALIZED COST	2993440
BENZENE REMOVAL FROM WASTE STREAM (Mg/Yr)	778
TOLUENE REMOVAL FROM WASTE STREAM (Mg/Yr)	622
PHENOL REMOVAL FROM WASTE STREAM (Mg/Yr)	467
TOTAL VOLATILE REMOVAL (Mg/Yr)	1867
COST EFFECTIVENESS OF VOLATILE REMOVAL ($/Mg)	1604
QUANTITY OF STREAM TREATED (kg/day)	426000
COST OF WASTE TREATMENT ($/kg waste)	0.0192516

Total capital cost includes construction fee (10 percent), contingency (15 percent), engineering (15 percent), and startup (1 percent).

Electricity at ($.05/kwh).

Capital recovery factor for 10-year lifetime at 10 percent.

TABLE A-2. ANNUALIZED COST ESTIMATES FOR THE PRETREATMENT OF WASTE STREAM 02.02.16 BY RESIN ADSORPTION

COST ELEMENT	ALL COSTS IN 1983 DOLLARS
RESIN ADSORPTION COLUMNS	240000
SOLVENT RECOVERY SYSTEM	600000
RESIN INVENTORY	1440000
FIELD COST	2280000
TOTAL INSTALLED COST	3214800
ANNUALIZED COSTS	
MAINTENANCE (5%)	160740
STEAM	276000
ELECTRICITY	12300
RESIN MAKEUP	40000
TAXES, INSURANCE, ADMINISTRATION (4%)	128592
OPERATING LABOR	126000
SOLVENT	13100
WATER	67400
PRODUCT RECOVERY CREDIT	- 562700
ANNUAL OPERATING COST	261432
CAPITAL RECOVERY (16.3%)	524012
TOTAL ANNUALIZED COST	785444
PHENOL REMOVAL FROM WASTE STREAM (Mg/Yr)	2558
TOTAL VOLATILE REMOVAL (Mg/Yr)	2558
COST EFFECTIVENESS OF VOLATILE REMOVAL ($/Mg)	307
QUANTITY OF STREAM TREATED (kg/day)	350000
COST OF WASTE TREATMENT ($/kg waste)	0.0061482

Total capital cost includes construction fee (10 percent), contingency (15 percent), engineering (15 percent), and startup (1 percent).

Electricity at ($.05/kwh).

Capital recovery factor for 10-year lifetime at 10 percent.

TABLE A-3. ANNUALIZED COST ESTIMATES FOR THE PRETREATMENT OF WASTE STREAM 02.02.12 BY BIOLOGICAL TREATMENT

COST ELEMENT	ALL COSTS IN 1983 DOLLARS
REACTORS	35500
FIELD COST	35500
TOTAL INSTALLED COST	50055
ANNUALIZED COSTS	
MAINTENANCE	
OPERATING LABOR	
ELECTRICITY	
TAXES, INSURANCE, ADMINISTRATION	
SUBTOTAL	5000
PRODUCT RECOVERY CREDIT	- 5000
BYPRODUCT DISPOSAL COST	0
ANNUAL OPERATING COST	0
CAPITAL RECOVERY (16.3%)	8159
TOTAL ANNUALIZED COST	8159
ACETALDEHYDE REMOVAL FROM WASTE STREAM (Mg/Yr)	120
TOTAL VOLATILE REMOVAL (Mg/Yr)	120
COST EFFECTIVENESS OF VOLATILE REMOVAL ($/Mg)	68
QUANTITY OF STREAM TREATED (kg/day)	2800
COST OF WASTE TREATMENT ($/kg waste)	0.0079833

Total capital cost includes construction fee (10 percent), contingency (15 percent), engineering (15 percent), and startup (1 percent).

Electricity at ($.05/kwh).

Capital recovery factor for 10-year lifetime at 10 percent.

TABLE A-4. ANNUALIZED COST ESTIMATES FOR THE PRETREATMENT OF WASTE STREAM 03.01.90 BY DISTILLATION

COST ELEMENT	ALL COSTS IN 1983 DOLLARS
DISTILLATION COLUMNS	250000
FIELD COST	250000
TOTAL INSTALLED COST	352500
ANNUALIZED COSTS	
MAINTENANCE (5%)	17625
UTILITIES	15000
TAXES, INSURANCE, ADMINISTRATION (4%)	14100
OPERATING LABOR	10000
PRODUCT RECOVERY CREDIT	- 50500
BYPRODUCT DISPOSAL COST	0
ANNUAL OPERATING COST	6225
CAPITAL RECOVERY (16.3%)	57458
TOTAL ANNUALIZED COST	63683
HEXANE REMOVAL FROM WASTE STREAM (Mg/Yr)	254
TOTAL VOLATILE REMOVAL (Mg/Yr)	254
COST EFFECTIVENESS OF VOLATILE REMOVAL ($/Mg)	251
QUANTITY OF STREAM TREATED (kg/day)	3482
COST OF WASTE TREATMENT ($/kg waste)	0.0501070

Total capital cost includes construction fee (10 percent), contingency (15 percent), engineering (15 percent), and startup (1 percent).

Electricity at ($.05/kwh).

Capital recovery factor for 10-year lifetime at 10 percent.

TABLE A-5. ANNUALIZED COST ESTIMATES FOR THE PRETREATMENT OF WASTE STREAM 03.04.14 BY EVAPORATION/CARBON ADSORPTION

COST ELEMENT	ALL COSTS IN 1983 DOLLARS
CARBON ADSORPTION COLUMNS (6 REQUIRED)	48000
EVAPORATOR SYSTEM	830000
CARBON/REFRIGERATION SYSTEM	45000
CARBON INVENTORY	720000
FIELD COST	1643000
TOTAL INSTALLED COST	2316630
ANNUALIZED COSTS	
MAINTENANCE (5%)	116000
STEAM	149000
ELECTRICITY	20000
OPERATING LABOR	66000
TAXES, INSURANCE, ADMINISTRATION (4%)	92665
PRODUCT RECOVERY CREDIT	-218000
BYPRODUCT DISPOSAL COST	0
ANNUAL OPERATING COST	225665
CAPITAL RECOVERY (16.3%)	377611
TOTAL ANNUALIZED COST	603276
VOLATILE REMOVAL FROM WASTE STREAM (Mg/Yr)	4355
TOTAL VOLATILE REMOVAL (Mg/Yr)	4355
COST EFFECTIVENESS OF VOLATILE REMOVAL ($/Mg)	139
QUANTITY OF STREAM TREATED (kg/day)	24000
COST OF WASTE TREATMENT ($/kg waste)	0.0688671

Total capital cost includes construction fee (10 percent), contingency (15 percent), engineering (15 percent), and startup (1 percent).

Electricity at ($.05/kwh).

Capital recovery factor for 10-year lifetime at 10 percent.

TABLE A-6. ANNUALIZED COST ESTIMATES FOR THE PRETREATMENT OF WASTE STREAM 01.02.02 BY ALKALINE CHLORINATION

COST ELEMENT	ALL COSTS IN 1983 DOLLARS
REACTORS, ELECTRICAL, PIPING, TANKS	219858
FIELD COST	219858
TOTAL INSTALLED COST	310000
ANNUALIZED COSTS	
MAINTENANCE (5%)	
CAUSTIC SODA AND CHLORINE GAS	
TAXES, INSURANCE, ADMINISTRATION (4%)	
OPERATING LABOR	
SUBTOTAL	250000
PRODUCT RECOVERY CREDIT	0
BYPRODUCT DISPOSAL COST	0
ANNUAL OPERATING COST	250000
CAPITAL RECOVERY (16.3%)	50530
TOTAL ANNUALIZED COST	300530
CYANIDE REMOVAL FROM WASTE STREAM (Mg/Yr)	3
TOTAL VOLATILE REMOVAL (Mg/Yr)	3
COST EFFECTIVENESS OF VOLATILE REMOVAL ($/Mg)	91070
QUANTITY OF STREAM TREATED (kg/day)	120000
COST OF WASTE TREATMENT ($/kg waste)	0.0068614

Total capital cost includes construction fee (10 percent), contingency (15 percent), engineering (15 percent), and startup (1 percent).

Electricity at ($.05/kwh).

Capital recovery factor for 10-year lifetime at 10 percent.

TABLE A-7. ANNUALIZED COST ESTIMATES FOR THE PRETREATMENT OF WASTE STREAM 02.02.21 BY WET OXIDATION

COST ELEMENT	ALL COSTS IN 1983 DOLLARS
PUMPS, HEAT EXCHANGER, COMPRESSOR REACTOR, VALVES, PIPING, ETC.	5815603
FIELD COST	5815603
TOTAL INSTALLED COST	8200000
ANNUALIZED COSTS	
MAINTENANCE	
OPERATING LABOR	
ELECTRICITY	
TAXES, INSURANCE, ADMINISTRATION (4%)	
SUBTOTAL	35000
PRODUCT RECOVERY CREDIT	0
BYPRODUCT DISPOSAL COST	0
ANNUAL OPERATING COST	35000
CAPITAL RECOVERY (16.3%)	1336600
TOTAL ANNUALIZED COST	1371600
PHENOL REMOVAL FROM WASTE STREAM (Mg/Yr)	985
TOTAL VOLATILE REMOVAL (Mg/Yr)	985
COST EFFECTIVENESS OF VOLATILE REMOVAL ($/Mg)	1392
QUANTITY OF STREAM TREATED (kg/day)	300000
COST OF WASTE TREATMENT ($/kg waste)	0.0125260

Total capital cost includes construction fee (10 percent), contingency (15 percent), engineering (15 percent), and startup (1 percent).

Electricity at ($.05/kwh).

Capital recovery factor for 10-year lifetime at 10 percent.

TABLE A-8. ANNUALIZED COST ESTIMATES FOR THE PRETREATMENT OF WASTE STREAM 02.02.14 BY OZONATION/RADIOLYSIS

COST ELEMENT	ALL COSTS IN 1983 DOLLARS
REACTORS	250000
OZONE GENERATOR/OXYGEN PLANT	8000000
FIELD COST	8250000
TOTAL INSTALLED COST	11632500
ANNUALIZED COSTS	
ELECTRICITY	613200
LAMP REPLACEMENT	15695
TAXES, INSURANCE, ADMINISTRATION (4%)	465300
OPERATING LABOR	200000
PRODUCT RECOVERY CREDIT	0
BYPRODUCT DISPOSAL COST	0
ANNUAL OPERATING COST	1294195
CAPITAL RECOVERY (16.3%)	1896098
TOTAL ANNUALIZED COST	3190293
BENZENE REMOVAL FROM WASTE STREAM (Mg/Yr)	736
TOLUENE REMOVAL FROM WASTE STREAM (Mg/Yr)	587
PHENOL REMOVAL FROM WASTE STREAM (Mg/Yr)	438
TOTAL VOLATILE REMOVAL (Mg/Yr)	1761
COST EFFECTIVENESS OF VOLATILE REMOVAL ($/Mg)	1812
QUANTITY OF STREAM TREATED (kg/day)	426000
COST OF WASTE TREATMENT ($/kg waste)	0.0205176

Total capital cost includes construction fee (10 percent), contingency (15 percent), engineering (15 percent), and startup (1 percent).

Electricity at ($.05/kwh).

Capital recovery factor for 10-year lifetime at 10 percent.

TABLE A-9. ANNUALIZED COST ESTIMATES FOR THE PRETREATMENT OF WASTE STREAM 05.01.03 BY PHYSICAL SEPARATION

COST ELEMENT	ALL COSTS IN 1983 DOLLARS
CENTRIFUGE,PIPING, AND ELECTRICAL	62411
FIELD COST	62411
TOTAL INSTALLED COST	88000
ANNUALIZED COSTS	
MAINTENANCE (5%)	4400
TAXES, INSURANCE, ADMINISTRATION (4%)	3520
OPERATING LABOR	3000
PRODUCT RECOVERY CREDIT	0
BYPRODUCT DISPOSAL COST	0
ANNUAL OPERATING COST	10920
CAPITAL RECOVERY (16.3%)	14344
TOTAL ANNUALIZED COST	25264
TOTAL VOLATILE REMOVAL (Mg/Yr)	0
QUANTITY OF STREAM TREATED (kg/day)	8200
COST OF WASTE TREATMENT ($/kg waste)	0.0084410

Total capital cost includes construction fee (10 percent), contingency (15 percent), engineering (15 percent), and startup (1 percent).

Electricity at ($.05/kwh).

Capital recovery factor for 10-year lifetime at 10 percent.

TABLE A-10. ANNUALIZED COST ESTIMATES FOR THE PRETREATMENT OF WASTE STREAM 02.01.03 BY SOLVENT EXTRACTION

COST ELEMENT	ALL COSTS IN 1983 DOLLARS
EXTRACTOR, DISTILLATION COLUMN PUMPS,PIPING	148936
FIELD COST	148936
TOTAL INSTALLED COST	210000
ANNUALIZED COSTS	
MAINTENANCE (5%)	
ELECTRICITY	
MAKEUP SOLVENT	
TAXES, INSURANCE, ADMINISTRATION (4%)	
OPERATING LABOR	
subtotal	40000
PRODUCT RECOVERY CREDIT	-60000
BYPRODUCT DISPOSAL COST	0
ANNUAL OPERATING COST	-20000
CAPITAL RECOVERY (16.3%)	34230
TOTAL ANNUALIZED COST	14230
PHENOL REMOVAL FROM WASTE STREAM (Mg/Yr)	260
TOTAL VOLATILE REMOVAL (Mg/Yr)	260
COST EFFECTIVENESS OF VOLATILE REMOVAL ($/Mg)	55
QUANTITY OF STREAM TREATED (kg/day)	16000
COST OF WASTE TREATMENT ($/kg waste)	0.0024366

Total capital cost includes construction fee (10 percent), contingency (15 percent), engineering (15 percent), and startup (1 percent).

Electricity at ($.05/kwh).

Capital recovery factor for 10-year lifetime at 10 percent.

TABLE A-11. ANNUALIZED COST ESTIMATES FOR THE PRETREATMENT OF WASTE STREAM 02.02.14 BY STEAM STRIPPING

COST ELEMENT	ALL COSTS IN 1983 DOLLARS
STEAM STRIPPING UNIT	907000
FIELD COST	907000
TOTAL INSTALLED COST	1278870
ANNUALIZED COSTS	
MAINTENANCE (5%)	63944
ELECTRICITY	62000
STEAM	3160000
TAXES, INSURANCE, ADMINISTRATION (4%)	51155
OPERATING LABOR	630000
PRODUCT RECOVERY CREDIT	- 154000
BYPRODUCT DISPOSAL COST	0
ANNUAL OPERATING COST	3813098
CAPITAL RECOVERY (16.3%)	208456
TOTAL ANNUALIZED COST	4021554
BENZENE REMOVAL FROM WASTE STREAM (Mg/Yr)	738
TOLUENE REMOVAL FROM WASTE STREAM (Mg/Yr)	578
PHENOL REMOVAL FROM WASTE STREAM (Mg/Yr)	219
TOTAL VOLATILE REMOVAL (Mg/Yr)	1535
COST EFFECTIVENESS OF VOLATILE REMOVAL ($/Mg)	2620
QUANTITY OF STREAM TREATED (kg/day)	426000
COST OF WASTE TREATMENT ($/kg waste)	0.0258637

Total capital cost includes construction fee (10 percent), contingency (15 percent), engineering (15 percent), and startup (1 percent).

Capital recovery factor for 10-year lifetime at 10 percent.

TABLE A-12. ANNUALIZED COST ESTIMATES FOR THE PRETREATMENT OF WASTE STREAM 02.02.20 BY AIR STRIPPING

COST ELEMENT	ALL COSTS IN 1983 DOLLARS
PACKED COLUMN AIR STRIPPING SYSTEM	145000
CARBON ADSORPTION COLUMNS (4 REQUIRED)	16000
CONDENSER/REFRIGERATION SYSTEM (10 TON)	15000
CARBON INVENTORY	10600
FIELD COST	186600
TOTAL INSTALLED COST	263106
ANNUALIZED COSTS	
MAINTENANCE (5%)	13155
STEAM	2400
ELECTRICITY	8150
OPERATING LABOR	15000
TAXES, INSURANCE, ADMINISTRATION (4%)	10524
PRODUCT RECOVERY CREDIT	-12530
BYPRODUCT DISPOSAL COST	0
ANNUAL OPERATING COST	36700
CAPITAL RECOVERY (16.3%)	42886
TOTAL ANNUALIZED COST	79586
CARBON TETRACHLORIDE REMOVAL FROM WASTE STREAM (Mg/Yr)	57
TOTAL VOLATILE REMOVAL (Mg/Yr)	57
COST EFFECTIVENESS OF VOLATILE REMOVAL ($/Mg)	1398
QUANTITY OF STREAM TREATED (kg/day)	12000
COST OF WASTE TREATMENT ($/kg waste)	0.0181702

Total capital cost includes construction fee (10 percent), contingency (15 percent), engineering (15 percent), and startup (1 percent).

Electricity at ($.05/kwh).

Capital recovery factor for 10-year lifetime at 10 percent.

TABLE A-13. HAZARDOUS WASTE PRETREATMENT: ESTIMATE OF PROCESS ECONOMICS FOR SELECTED CANDIDATE PRETREATMENT TECHNIQUES[a]

Technology	Basis of estimate	Estimated unit cost, January 1983 dollars	Estimated cost effectiveness, January 1983 dollars
Adsorption, carbon	WET model stream 02.02.14 (quench blowdown from ethylene production). 17,751 kg/hr @ 0.4 wt. % toluene, 0.3 wt. % phenol, 0.5 wt. % benzene. 330 day/yr operation @ 24 hr/day. 100% removal of toluene, phenol, and benzene.	\$0.0192/kg treated	\$1.60/kg organic removed
Adsorption, resin	WET model stream 02.02.16 (Decanter wastes from phenol production). 14,583 kg/hr @ 2 wt. % phenol, 90 wt. % water. 330 day/hr operation @ 24 hr/day. 100% removal of phenol.	\$0.0061/kg treated	\$0.31/kg phenol removed
Biological treatment	WET model stream 02.02.12 (Heavy ends from ethylene oxide production) 15.8 percent acetaldehyde produced at 2,800 kg/day.	\$0.0080/kg treated	\$0.068/kg organic removed
Distillation	WET model stream 03.01.90 (spent solvents). 454 kg/hr @ 80 wt. % toluene, 20 wt. % hexane. 2,800 hr/yr operation. Overhead product @ 95 mol % hexane, bottoms product @ 95 mol % toluene.	\$0.05/kg treated	\$0.251/kg organic removed
Evaporation (with carbon adsorption)	WET model stream 03.04.14 (distillation cut from acetaldehyde production by ethylene oxidation). 24,000 kg/day. 16.2 wt. % acetaldehyde, 11.7 wt. % chloroacetaldehyde, 2 wt. % chloroform, and 2 wt. % formaldehyde. 330 day/yr operation @ 24 hr/day. 100% removal of all species.	\$0.069/kg treated	\$0.14/kg organic removed
Oxidation, chemical	10^6 gal/day of coke plant wastewater containing phenol and ammonia. 350 day/yr operation @ 24 hr/day.	\$0.0069/kg treated	\$91/kg cyanide removed
Oxidation, wet	WET stream 02.02.21 (acetophenone column separator from phenol production by cumene hydroperoxide). 12,500 kg/hr contain 1 wt. % phenol in aqueous soln. 350 day/yr operation @ 24 hr/day.	\$0.0125/kg treated	\$1.39/kg phenol removed

(continued)

Footnotes at end of table.

TABLE A-13 (continued)

Technology	Basis of estimate	Estimated unit cost, January 1983 dollars	Estimated cost effectiveness, January 1983 dollars
Ozonation	WET model stream 02.02.14 (quench blowdown from ethylene production). 17,751 kg/hr @ 0.4 wt. % toluene, 0.3 wt. % phenol, and 0.5 wt. % benzene. 350 day/hr operation @ 24 hr/day. 95% removal of toluene, phenol, and benzene.	\$0.02/kg treated	\$1.81/kg organic removed
Physical separation via bowl centrifuge	WET model stream 05.01.03 (sludge from tin plating mill operations). 8,200 kg/day @ 10 wt. % solids. 350 day/yr operation @ 24 hr/day. ~99% solids removal.	\$0.008/kg treated	b
Solvent extraction	WET model stream 02.01.03 (phenol-formaldehyde solution from plastics production) 1,600 kg/hr @ 5 wt. % phenol, 2 wt. % formaldehyde, 90 wt. % water. 350 day/yr operation @ 24 hr/day.	\$0.0024/kg treated	\$0.055/kg phenol removed
Stripping, air (with carbon adsorption)	WET model stream 02.02.20 (caustic scrubber effluent from perchloroethylene and carbon tetrachloride production). 500 kg/hr @ 1.3 wt. % CCl_4 and 88.8 wt. % water. 330 day/hr operation @ 24 hr/day. 100% removal of CCl_4.	\$0.018/kg treated	\$1.40/kg CCl_4 removed
Stripping, steam	WET model stream 02.02.14 (quench blowdown from ethylene production). 1,600 kg/hr @ .4 wt. % toluene, .3 wt. % phenol, .5 wt. % benzene. 350 day/yr operation @ 24 hr/day.	\$0.038/kg treated	\$0.154/kg organic recovered

[a] Capital costs are annualized at 10% over 15 years.

[b] This process is used in combination with other pretreatment processes.

APPENDIX B

ATMOSPHERIC EMISSION FROM COOLING TOWERS

There is substantial incentive on the part of production facilities with hazardous aqueous streams to incorporate maximum recycle and reuse of plant wastewaters into the design of new or existing production facilities. The incentive for "zero liquid discharge" arises from (1) expectation of fairly stringent regulatory requirements to be imposed on the industry, and (2) conservation of water resources. Many proposed synfuels facilities have already indicated the choice of zero liquid discharge schemes in their plant designs. Included in this category are the Hampshire Energy Project, the Great Plains Gasification Project, the Breckinridge County H-coal Project, the Newman, Kentucky, SRC-I Project, and the Morgantown, West Virginia, SRC-II Project. Cooling towers are used at coke oven byproduct plants, petroleum refineries, pulp and paper plants, and other facilities.

One approach to accomplishing the zero discharge objective involves the reuse of process condensates as cooling tower makeup water. However, these condensates are often heavily laden with both inorganic and organic impurities, depending on the process. These contaminants can cause both operational and environmental problems in cooling tower operation. Typical wastewater analyses of synfuel facilities are shown in Tables B-1 and B-2.

In addition to the compounds identified in Tables B-1 and B-2, Mohr and King have identified dimethylhydantoin and related polar compounds in coal gasification condensate water.[1] A significant fraction of the chemical oxygen demand (COD) in many condensate waters is composed of compounds that are more polar than phenol. These polar compounds are not removed by common solvents such as diisopropyl ether or methyl isobutyl ketone. In addition, these compounds are not extracted by methylene chloride so they are not successfully analyzed by the gas chromatography/mass spectrometry (GC/MS) analytical techniques conventionally used to study these streams.

TABLE B-1. TYPICAL WASTEWATER ANALYSES OF SYNFUEL FACILITIES

	Gasifier Gasifier				
Pollutant	RTI Range[a] Illinois No. 6 (μg/L)	Lurgi[b] Illinois No. 6 (μg/L)	Lurgi (Calculated)[c] North Dakota Lignite (μg/L)	GFETC[d] N. Dakota Lignite (μg/L)	Chapman[e] VA Bituminous (μg/L)
Phenolics	9.5E5-3.9E6	2.2E6	2.6E6	5.5E6	2.2E6
COD	2.2E7	1.0E7	1.3E7	3.2E7	2.0E7
Thiocyanate	2.7E5	6.5E4	8.5E4	1.2E5	7.8E5
Cyanide	5.9E2-3.5E3	3.0E3	4.6E4	1.8E3	1.3E4
Ammonia	4.0E6-1.4E7	2.0E6	2.9E6	7.7E6	6.7E6
Chloride	2.2E6-6.7E6	1.4E4	NA	NA	NA
Phenol	4.6E4-2.9E6	NA	NA	4.5E6	NA
Cresols	1.1E5-1.5E6	NA	NA	NA	NA
C_2-Phenols	6.3E4-3.7E5	NA	NA	NA	NA
TOC	7.7E6-8.9E6	NA	4.2E6	1.1E7	6.3E6
Sulfide	7.8E4-2.5E6	2.4E4	NA	NA	NA
Total sulfur	NA	NA	1.4E5	NA	NA
BOD_5	NA	NA	5.6E6	NA	NA
Other organics	NA	NA	2.3E5	NA	NA
TDS	NA	NA	2.5E6	NA	NA
TSS	NA	NA	3.0E5	NA	NA

[a] Laboratory-scale fixed-bed, airblown gasifier.

[b] At inlet to tar separator ("Trials of American Coals in a Lurgi Gasifier at Westfield, Scotland," ERDA R&D Report No. 105 (1974).

[c] Personal communication, U.S. Environmental Protection Agency, IERL, Research Triangle Park, NC.

[d] Luthey et al., 1981.

[e] Data from the University of North Carolina, Chapel Hill, NC.

COD = Chemical oxygen demand.
TOC = Total organic demand carbon.
TDS = Total dissolved solids.
TSS = Total suspended solids.
BOD_5 = Biochemical oxygen demand.
NA = Not available.

TABLE B-2. UNTREATED WASTEWATER COMPOSITION--SRC-I AND SRC-II

Chemical	SRC-I[a] (mg/L)	SRC-II[b] (mg/L)
Methylindane	15.0	-
Tetralin	0.1	0.1
Naphthalene	5.0	-
Dimethylnaphthalene	0.3-2	-
2-Isopropylnaphthalene	0.7	-
1-Isopropylnaphthalene	2.0	-
Biphenyl	0.2	0.2
Acenaphthalene	<0.1	-
Dimethylbiphenyl	0.2-0.5	-
Dibenzofuran	0.6	0.5
Xanthene	0.1	0.1
Dibenzothiophene	1.5	-
Methyldibenzothiophene	<0.1	-
Thioxanthene	0.1	-
Fluorene	0.3	0.3
9-Methylfluorene	0.3	-
1-Methylfluorene	0.2	-
Anthracene/Phenanthrene	1.1	0.36
Methylphenanthrene	0.2-0.3	-
C_2-Anthracene	0.05	-
Fluoranthene	0.4	0.11
Bihydropyrene dihydropyrene	<0.05	-
Pyrene	0.6	0.25
Dimethyldibenzothiophene	<0.05	-
Acenaphthene	-	<0.1
Diphenylmethane	-	0.3
Benz(a)anthracene	-	0.01
Triphenylene	-	0.002
Methylbenz(a)anthracene	-	0.003
Benz(a)pyrene	-	<0.003
Benz(e)pyrene	-	<0.002
Benzo(g,h,i)perylene	-	0.004
Titanium	-	<3.0
Vanadium	-	<0.25
Aluminum	-	<2.0

See notes at end of table. (continued)

TABLE B-2 (continued)

Chemical	SRC-I[a] (mg/L)	SRC-II[b] (mg/L)
Arsenic	-	0.03
Selenium	-	2.5
Mercury	-	0.05
Nickel	-	0.12
Cadmium	-	<0.006
Barium	-	<0.2
Lead	-	0.2
Silver	-	0.05
Zinc	-	0.5
Boron	-	12
Fluoride	-	70
Copper	-	0.11
Beryllium	-	0.013

- No data.

[a] Data from Table 3, J.S. Fruchter, M.R. Peterson, J.C. Laul, P.W. Ryan, High Precision Trace Element and Organic Constituent Analysis of Oil Shale and Solvent Refined Coal Materials, Battelle Pacific Northwest Labs, BNWL-SA-6001, 1976, 31 pp.

[b] Data from Solvent Refined Coal-II Demonstration Project-Final Environmental Impact Statement, DOE/EIS-0069/V2 (January 1981).

Liquid chromatography was used to identify the hydantoins in the wastewater sample.[1] A solvent exchange process to replace the water with isopropanol was used to prepare the sample for the liquid chromatography. The presence of the dimethylhydantoin and related compounds in isopropanol permits the identification of the compounds by GC/MS.

In one of the plans[2] to use cooling towers to treat water from coal gasification plants and zero discharge basis, 67 percent of the wastewater would be returned to the atmosphere as water vapor through evaporation, 24 percent would be consumed by the synthesis gas reactions, 2.5 percent would be present in the ammonia byproduct, and approximately 6.5 percent would be present in the solid waste products and cooling tower drifts. Isopropyl ether was proposed to recover phenols as a byproduct. Carbon dioxide (CO_2) would be stripped from the water, and the ammonia stripped from the water would be recovered as a byproduct.

Gloyna has described a program of water management that uses cooling towers for concentrating refinery wastewater.[3] The concentration of phenols and similar organic materials was reduced substantially. Although the relative mechanisms for removal of organic materials were not determined, the mechanisms were thought to involve a combination of biodegradation, precipitation, absorption, and volatilization. In 1 year of cooling tower operation, the only blowdown was the removal of sludges from the bottom of the tower. The fouling of heat exchangers and cooling tower equipment as a result of biological buildup did not occur, and it was postulated that the abnormally large amounts of heavy metals kept the biological growth in check. The sludge that was produced in the bottom of the cooling tower resisted aerobic digestion and contained a high concentration of heavy metals. The cooling tower thus served as a wastewater treatment process, with an oily sludge as the only liquid effluent from the process.

Fleischman described the phenol biooxidation at the Sun Oil's Toledo refinery.[4] Sodium hexametaphosphate was used as a corrosion inhibitor and a microbial nutrient for biological oxidation. Due to the biological oxidation in the cooling tower, the dissolved oxygen concentration in the cooling water was less than 2 ppm. Fouling and/or corrosion of the heat transfer surfaces was possible when phenol concentrations in the cooling water were greater than 5 ppm. At the Toledo refinery, the heat exchangers were backflushed daily. In Exxon laboratory tests, it was concluded that biofouling should not be a problem with 44 ppm biochemical oxygen demand (BOD) and 75 ppm COD in the circulating water in the absence of ammonia.

In addition to the proposed use of industrial wastewater as cooling tower makeup, treated municipal wastewater has also been considered for use in cooling towers. Even after biological oxidation, sewage is highly nutrient-rich. Slime and algae growth are serious problems when municipal wastewater is used in a cooling tower.[5] Disinfection by chlorination and frequent shock treatment was considered normally adequate. Biocide was required at 1.5 to 10 times the level for freshwater. Phenol reduction in a cooling tower has been reported when chlorination was used for slime control. A tertiary treatment of lime precipitation was proposed to permit the water to obtain high concentrations. Biological treatment with high phosphate removal was recommended for consideration. Water with a high silica content required lime treatment whether or not phosphate was removed, but the treatment would be easier if the approved biological treatment were used.

Operational problems associated with cooling towers operating as part of a wastewater treatment system include corrosion, scale formation, fouling, and foaming. Cooling tower water by nature is likely to be corrosive. A portion of the water has been evaporated, thus resulting in a concentration of inorganic constituents, and the water is normally saturated with oxygen as a result of its contact with air. These factors tend to enhance corrosion, which can severely limit the life of heat exchangers and other process equipment. The high levels of inorganic materials can also cause scale formation, in that concentrations can exceed solubility limits at the surface temperatures of heat exchangers. Salts and other materials precipitate out, cover the heat transfer surfaces, and severely limit the rates of heat transfer. Similarly, organic materials and biological slime can blanket the heat transfer surfaces and also severely limit the rates of heat transfer. Organic materials present in the cooling tower can cause foaming, which limits heat and mass transfer and thus severely interferes with the operating effectiveness of the cooling tower. Moreover, foam in excessive quantities exiting from the top of the cooling tower is a troublesome environmental problem. Acceptable loadings for mineral contaminants for satisfactory tower operation are fairly well established; those for organic loadings are virtually unknown.

In a water reuse study sponsored by the petroleum industry, Grutsch and Griffin (1979) report that even at six or more cycles of concentration in the cooling tower, the residual ammonia in recirculating cooling water is typically about equal to or less than the ammonia content of the makeup water.[6] In addition, major reductions in total organic carbon and phenolics are achieved. About 50 percent of the organic carbon was removed. Based on the rates of biological oxidation, biological oxidation was not a significant mechanism for removal of ammonia and/or organics in typical cooling tower operation. To verify the mechanisms of ammonia or organic removal, additional tests were run after sterilizing the recycle water with a copper biocide and under both slightly alkaline and acidic pH conditions. The test results after sterilizing the systems were consistent with the results from the previous testing. Therefore, it was concluded that biological oxidation was not an important removal mechanism for ammonia and organic losses in the cooling tower. In addition, the rate of removal of phenolics was approximately the same at slightly acidic and alkaline conditions. It was concluded in the API study that, since air stripping was the predominant contaminant removal mechanism, an effective treatment of refinery wastewater makeup would usually be necessary to control air emissions from cooling towers.[6]

In a similar study by the Georgia Craft Company,[7] evaluations were made in a laboratory cooling tower to provide proof that biological action was a very minor treatment mechanism. Two identical cooling towers were constructed with one tower operating on airstripping alone and the other being seeded with bacteria and fed with nutrients to operate with both airstripping and biological action. Experiments were performed when the biological material growth had covered the tower packing surface to the extent that portions of growth would slough off and fall to the basin. Biological action contributed only 4 to 12 percent more BOD reduction than did stripping alone. The effect of biological action was dependent upon the flow rates of liquid and gas and appeared to increase with increasing liquid-to-gas ratio. Biological action in simultaneous operation with stripping produced greater BOD removal since the biological reactions could attack the nonvolatile portion of the BOD-producing compounds. It was concluded that the amount of increased treatment due to biological action could not appear to justify the operational costs encountered to achieve the reductions used.[7]

The microorganisms in a cooling tower were projected to remove 90 percent or more of the phenols and reduce effluent organic carbon and oxygen demand, but this mechanism was reportedly inhibited by sulfide because the sulfides apparently killed the phenol-oxidizer microorganisms.[8] Therefore, it was recommended that the water should be diverted from the cooling system when sulfide levels exceed 2 ppm in the wastewater.[8]

Cooling towers in the coke byproduct recovery industry are used to cool direct-contact water that has been contaminated with organics from the process stream. Some organics, primarily naphthalene, are removed from the water by either physical separation of solid naphthalene or by passing the water through a tar-bottoms reservoir to dissolve the naphthalene and other organics. An initial environmental assessment of coke oven byproduct plants measured a benzene concentration of 15.8 mg/sm^3 above a direct water cooling tower; in addition, other organic compounds were identified.[9] Emission tests were conducted at three other byproduct plants and yielded emission factors of 270 g benzene/mg coke for direct-water cooling towers and 70 g banzene/mg coke by tar-bottom cooling towers. Emission rates varied from 12 lb/h for the tar bottom to 73 lb/h for the direct water.[10] [11] [12] Other relevant test data are summarized in Table B-3.

These data from industrial cooling towers in coke byproduct recovery plants demonstrate that environmentally significant organic emissions can be produced by cooling towers using water containing only a few parts per million contaminant. Solvent extraction, followed by ammonia stripping, should substantially reduce the potential cooling tower emissions from previously contaminated water from coal gasification plants. One of the objectives of this investigation was to determine the type and extent of wastewater pretreatment necessary to eliminate or reduce to acceptable

TABLE B-3. BENZENE EMISSIONS FROM COOLING TOWERS

Location	CF&I Pueblo, CO	U.S. Steel Fairless Hills, PA	Beth, S.C. Bethlehem, PA
Benzene emissions (lb/h)	11.9	70.2	73.4
Stack velocity (ft/min)	1,430-1,780	1,200-1,700	860-905
SCFM	384,000-470,000	255,000-369,000	432,000-456,000
Cold well, ppm benzene	7.5	1.0	3.5
Hot well, ppm benzene	68	48	6.8
Type of cooling tower	tar bottom	direct water	direct water
Stack area (ft^2)	314	227	532

levels any atmospheric pollutant releases from cooling towers receiving contaminated makeup water.

In addition to atmospheric emissions from organics being evaporated into the cooling tower exhaust, water droplets can be ejected from the cooling tower as entrained water droplets. Vertical air velocity through cooling towers typically varies from 300 to 700 ft/min.[13] A baffle or drifting eliminator system is placed between the water distribution system and the air discharge point to minimize the dispersal of entrained water droplets. Drift elimination is essential for the conservation of water, the retention of chemical treatment in the cooling water, the prevention of damage by the chemical additives in the surrounding area, and for environmental protection. A common method of trying to improve cooling tower performance is to increase the air velocity by increasing the fan power and pitch angle. This often causes increased drift loss because the eliminators are not designed for these process conditions.[13] An acceptable level of drift elimination, generally considered satisfactory, is "not in excess of 0.2 percent."[13]

A continuous precipitation of drizzle in the neighborhood is potentially possible with nearly all types of cooling towers. The mist lost in a fog plume is approximately .007 percent of the circulating water rate.[14] The visible plume does not cause a nuisance since the rate of small particles is low. Condensation with mist formation takes place as soon as the exit air begins to mix with the atmospheric air. Drizzle begins to precipitate at a certain distance from the tower. As the air from the cooling tower is further mixed with the surrounding air, the drizzle precipitation stops. As still more air is added, the fog begins to reevaporate and finally vanishes.[14] It has been suggested that a combination of wet/dry cooling tower can significantly reduce the water consumption and effluent volume from a cooling tower compared to a conventional cooling tower.[15] Also, the direct/indirect heat exchange can result in the elimination of visible plume from the cooling tower exhaust.[15]

Another environmental aspect of cooling tower emissions--concerning emissions of pathogenic bacteria--involves somewhat different considerations than stripping or chemical and biological oxidation. Although the oxidative processes may be insignificant in reducing liquid phase concentrations (compared to stripping), they may be highly significant in the production of pathogenic organisms or partially oxidized materials in the vapor and drift.

It is noted that cooling towers have been heavily implicated in outbreaks of Legionnaires' disease by providing a breeding ground for Legionella pneumophila, the bacteria responsible for the disease.[16] It is believed that human exposure to the bacteria is often caused by humans coming into contact with bacteria-laden drift from contaminated cooling towers. When the towers (invariably institutional towers) have been put on a regular disinfection schedule, the legionellosis outbreaks have ceased. Towers receiving organically contaminated makeup water in synfuels facilities, once infected, may harbor these bacteria since the temperature, nutrients, and oxygen needed for bacterial survival and population growth are more than adequate and since disinfection by chlorination will probably be excluded to avoid formation of toxic chlorinated organics. This problem is currently under consideration at the Department of Energy's Savannah River Laboratory under Electric Power Research Institute (EPRI) sponsorship.

Environmental concerns center around atmospheric emissions of dissolved contaminants as a result of air stripping and entrainment, salt deposition on neighboring land areas from evaporation of cooling tower drift, and possible entrainment of pathogenic bacteria such as Legionella pneumophila, Salmonella, Yersinia, Arizona, and Shigella. These bacteria are not necessarily present in synfuel cooling tower water, but the warmth and air circulation in cooling towers provide opportunity for bacteria present in the atmosphere to be captured by the water and grow. Bacteria in the small cooling tower droplets could travel for many miles before settling after the water evaporates from the small droplets. Naegleria, a pathogenic amoeba that causes fatal illnesses, has not been isolated in cooling tower drift, but has been found in thermally polluted waters containing cooling tower blowdown.

Cooling towers potentially can produce a large amount of mist from their vents, particularly the older designs.[17] Drift eliminators can reduce the major apparent problems of drift such as salt deposits, the production of fog, and corrosion, but they have little or no effect on the emission of small aerosol particles of biological significance. The small aerosol particles exhibit a negligible settling velocity and can travel long distances downwind. Some bacteria, such as escherichia coli do not survive well in the cooling tower environment. Also, gram negative enteritic pathogenic bacteria are not found in large numbers at cooling towers. Seventy-five bacterial colonies were isolated from petrie plates exposed to the vent of a cooling tower. Forty percent of the isolates were gram positive rods, cocci, or yeast. The remaining 60 percent were gram negative rods.[17]

Viruses are present in sewage and sewage-polluted streams that could be used for cooling tower makeup water. These viruses are of particular concern since they are resistant to chlorination. The authors conclude that the potential public health hazard from microbial aerosol existing in a cooling tower plume was difficult to estimate.[17] Under certain conditions individuals may be subject to some risk.

Air conditioning cooling towers have been linked to deaths from the bacteria legionella.[16] There were 88 cases of legionellosis in the town of Burlington, Vermont, in 1980. Thirty-four people were killed by this disease in the Philadelphia outbreak of 1976, and more than 34 people have died since 1977 in Burlington. The outbreak of Legionnaires Disease was linked to the Given tower at the University Medical Center. There were no cases of Legionnaires Disease while the Given tower was being treated with chlorine, but the disease reappeared after the chlorination was stopped. After the chlorination was resumed, the number of cases of Legionnaires Disease dropped off again. Most of the disease victims had been within 1,000 ft of the tower. Legionella thrive in warm water and like the company of algae. They seem to derive special protection against desiccation in air transport when they travel with algae. Carl Fliermans, who studied legionnella at E.I. du Pont Savannah River Laboratory, was reported to have said that it was possible for bacteria in an aerosol to travel half a mile and produce an infection.[16]

Chlorine has been shown to be effective in disinfecting cooling towers contaminated with legionnella. Unfortunately, the presence of chlorine can increase the corrosion of cooling tower components. One method for potential decontamination of cooling towers is to use ozone treatment in cooling towers. Ozone treatment does not have the problems that chlorine residual and trihalomethanes have in wastewater discharges. Also, ozone is apparently effective in controlling chemical scaling.

One manufacturer of ozone treatment devices states that ozone can be used as a sole source of treatment for the control of biofouling and chemical scaling in low temperature heat exchange systems and that no blowdown is required.[18] Minimizing the blowdown volume is of great value where the blowdown must be treated before ultimate discharge. Several air conditioning cooling systems treated with ozone were performing satisfactorily with respect to the control of biofouling corrosion and chemical scaling.[18] These systems were operated at very high cycles of concentration where little makeup water was required and little blowdown generated. Makeup water for cooling towers of electrical utilities can come from a number of active biological sources including sewage effluents, rivers, and freshwater runoff. A concern has been expressed regarding biological aerosol generation from these cooling towers.

Algae growth at the time of the installation of an ozone system was extensive.[19] Heavy-scaled deposits were on the cooling tower slats. Operation of the cooling tower with the ozonator producing a steady stream of ozone in the cooling tower lasted 1,080 hours. During this period of operation with no blowdown, the water in the tower became crystal clear, the algae disappeared, and the scales started flaking off the slats. The corrosion rates for the metal coupons were very low during the ozonation run. The mechanism for the increased calcium carbonated solubility in the water after ozone treatment could be due to the formation of calcium bicarbonate, or the dilute nitric acid produced by mixing nitrogen in the ozonator. It is reported that oxidation of organic impurities begins immediately.[19] By the time the ozonated water reaches the basin sump, most of the microorganism kill has been accomplished.

To summarize the previous information in this chapter, atmospheric emissions from cooling towers are potentially significant. In one of the previous investigations involving the treatment of selected aqueous kraft mill wastes in a cooling tower,[21] organics were removed predominantly by air stripping, with biological activity playing only a very minor role. The results of this study may have been somewhat compromised in that there was no pretreatment to remove reduced sulfur compounds, which are known to inhibit biodegradation. Nevertheless, the results do point to a significant potential for atmospheric emissions of wastewater contaminants since 25 to 30 percent of the BOD reduction was attributed to physical stripping of volatile components. Similarly, Grutsch and Griffin[6] reported 80 percent removal of phenol and 50 percent removal of TOC in a cooling tower fed with treated refinery sour water where no biological activity occurred. Harpel and James[20] show examples of chemical plant wastewaters treated in cooling towers and indicate that most of the organic matter (mainly benzene and toluene) vaporized over the tower at three and four cycles of concentration.

These investigations seem to confirm the following conclusions:

1. Air stripping and aerosol formation are the predominant mechanisms for removal of synfuels contaminants from the liquid phase.
2. Chemical and biological oxidation are much less significant in liquid phase cleanup.

The following questions, however, remain of major environmental concern:

1. What chemical species are present, and in what quantities, in the vapor and aerosol emissions from cooling towers?
2. To what extent do these species result from (a) simple stripping, (b) chemical oxidation, or (c) biological oxidation?
3. What is the likelihood of pathogenic bacteria being present in the atmospheric emissions?

Again, acceptable loadings for mineral contaminants are fairly well established; those for organic loadings are uncertain but have been suggested. Probable cooling water composition for the Lurgi gasification process and suggested cooling water limits are given in Tables B-4 and B-5.

Normally, cooling towers are regarded as devices in which a single process is occurring--simple evaporative cooling of a liquid stream. However, the presence of mineral contaminants introduces potential environmental problems associated with the release of these contaminants to the

TABLE B-4. CALCULATED ESTIMATE OF EXTRACTED STRIPPED LURGI WASTEWATER COMPOSITION (Produced from gasification of North Dakota Lignite)

	mg/L (except pH)
Phenols	160
BOD	1,470
COD	6,740
TOC	2,320
Ammonia	150
Cyanide	1.7
Thiocyanate	85
Fatty acids	190
TDS	2,460
Sulfides	0
Total sulfur	95
Sulfite & sulfate	150
Tar & oil	50
pH	9.5

SOURCE: Personal communication, U.S. Environmental Protection Agency, IERL, Research Triangle Park, NC.

TABLE B-5. SUGGESTED LIMITS ON MAKEUP TO A COOLING TOWER

Phenols	100
BOD	1,000
COD	>2,000
Ammonia as N	100
H_2S	2

SOURCE: Hicks, R. E., et al., Wastewater Treatment in Coal Conversion, EPA-600/7-79-113 (June 1979).

neighboring air. Typical problems include crop damage and corrosion of machinery as a result of salt deposition. Further introduction of organic contaminants--as in synfuels condensates--greatly complicates the possible emissions. A number of the ingredients of synfuels condensates--notably phenols, ammonia, and sulfur compounds--are not only toxic but volatile as well. One would expect these materials to be stripped from the wastewater very actively in normal cooling tower operation. Entrainment, chemical oxidation, and biological oxidation can also be expected to occur within the cooling tower, with environmental emissions as indicated:

Stripping -- Vapor phase contaminant emission

Entrainment -- Aerosol contaminant emission

Chemical oxidation -- Vapor and aerosol emissions of oxidized material

Biological oxidation -- Vapor and aerosol emissions of oxidized material, metabolites, and possibly pathogenic bacteria

Available information, as well as conventional wisdom, suggest that stripping and aerosol formation are the dominant mechanisms of concern, with characteristic times* on the order of minutes. Wet oxidation and biological treatment are probably much less important in the cooling tower environment, with characteristic times* on the order of days.

A few studies have sought to encourage bioactivity in the tower to accomplish simultaneous cooling and water treatment. Most of these studies, however, fail to provide convincing evidence of significant contaminant removal by chemical or biological activity. The best documented study of the successful operation of such practice is probably that by the Sun Oil Company refinery in Toledo, Ohio, using refinery wastewater.[21] Phenol, COD, and TOC removals were found to be 99.4 to 99.9 percent, 62 to 93 percent, and 67 percent, respectively. Another study using refinery-stripped sour water gave 92.0 to 97.2 percent removal of phenolics,[22] while a third study using secondary sewage effluent showed phenolic, BOD, and COD removals of 98, 77, and 80 percent, respectively.[23] These studies indicate the feasibility of removing organic water contaminants in cooling towers, albeit at relatively low organic loadings. However, no information concerning volatile organic emissions from the towers was collected so the fraction of organic removal due to physical stripping, compared to that removed by bio-oxidation, could not be determined.

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*Rigorously, the characteristic time is that required for a process to proceed $1/e^{th}$ of the way to equilibrium.

The emissions of volatile organic materials from a cooling tower can be predicted to some extent by mathematical modeling. The evaporation of water into the air involves some of the same transport mechanisms as the evaporation of volatile organics. The following theoretical analysis of stripping from cooling towers is borrowed from a publication of the U.S. Environmental Protection Agency, Treatment of Selected Internal Kraft Mill Wastes in a Cooling Tower, PB 208 217.[7] The nomenclature is identical to that used in the sited report, and the text has been edited in this section to make the discussion more relevant to emissions from cooling towers utilizing coal gasifier wastewater. A mathematical description of the process of volatilization of air from cooling towers was obtained by first identifying the most significant variables in the airstripping process. These variables are identified below:

R = Fraction removal of volatile component in feed water to the cooling tower

x = Concentration of volatile component in liquid phase

B = Blowdown rate

G = Gas rate

L = Total liquid rate to tower (feed plus recirculation)

t_1 = Inlet temperature of water in tower

t_{wb} = Wet bulb temperature of entering air.

The transport process is simplified due to the low concentration of volatile materials involved. Under these conditions, Henry's law is assumed to be valid, and for a gas-liquid equilibrium system the concentration of a gas phase volatile component (y) could be described as being directly proportional to the liquid phase concentration (x). Thus,

$$y = k_h x \, . \tag{B-1}$$

In a cooling tower, equilibrium is not attained between the contacting gas and liquid phases, but equilibrium is approached to approximately the same degree at all points along the height of the cooling tower. A small volume of liquid progressing through the tower would therefore not be in equilibrium with the surrounding gas phase, but the gas phase composition of the transferring component at any height, x, in the column would be

$$y_z = k \; k_h x_{LZ} \, . \tag{B-2}$$

Under constant operating conditions, the amount of volatile material removed by the system is

$$T_{xT} = K \; L x_{L1} \, . \tag{B-3}$$

The constant, K, was defined as the stripping constant and is independent of the concentration level of the volatile BOD-producing materials in the wastewater being treated. The constant is dependent, however, on variations of the chemical makeup of the volatile compounds, the tower packing material, the temperature, and the gas-to-liquid ratio.

The constant, K, as defined, represented the transfer of volatile materials to the air from a fixed volume of liquid as it passed once through the tower. Increased recirculation of wastewater through the tower would increase the number of times a given volume of wastewater would pass through the tower and would, therefore, affect the ultimate treatment accomplished on this volume of liquid. A series of material balances on the major streams shows that treatment in the tower can be described with the relationship

$$R = K \, (1 + B/L_1)/(K + B/L_1) \; , \tag{B-4}$$

and K could be evaluated from the equation

$$K = 1 - X_{L1}/X_{L2} \, . \tag{B-5}$$

The heat and mass transfer processes could be analyzed by starting with the first principles of classical theory, such as described by Treybal[13] or Bird et al.[14] The classical differential equations in a packed tower were

$$dh = dz/HTU_H (h^* - h) \tag{B-6}$$

and

$$dy = dt/HTU_M (y^* - y) \, , \tag{B-7}$$

which could be transformed with the aid of heat and material balances over a section of the tower to

$$dt = dz/HTU_H \cdot 1/(L/G) [h^* - L/G (t - T_1) + h_1] \tag{B-8}$$

$$dx = dz/HTU_M \cdot 1/(L/G) [y^* - (L/G) (x - x_1)] \, . \tag{B-9}$$

These equations had to be solved simultaneously because y^* is very temperature-dependent for volatile compounds such as methanol.

By numerically evaluating these equations, it was learned that x_2/x_1, and thus K, was independent of the absolute concentration of dilute volatile materials of interest in this study. The result was regarded as highly significant in validating the assumptions used in defining K and in applying K in design calculations.

The primary application of this theoretical work was to determine what degree of treatment could be expected from conventional cooling tower equipment when operated on wastewater as was done in this study. The theory is applied to the data described in the following section. It can be seen from this equation that a log-log plot of x versus $(1 - aQt/V_o)$ resulting in a straight line would have a slope of $(K - a)/a$ from which K may be calculated.

Experimental Technique--A very effective experimental method involving nonequilibrium conditions was devised for laboratory studies of stripping. The experimental procedure consisted of charging the cooling tower basin with a known volume of wastewater to be tested and then circulating the liquid through the tower and observing the change of concentration with time. No feed was added to the tower after filling the basin and no blowdown was withdrawn. Operation in this manner was time-dependent and would not appear to embrace a simple mathematical description. It resulted, nevertheless, that a simple balance of the material entering and leaving the system would give an equation that would accurately and quickly determine the stripping constant, K. From the ultimate BOD content that could be reached by prolonged treatment, the procedure gave directly the amount of volatile BOD in the original wastewater.

$$x_2 = x_1 \quad 1 - {\frac{aQt}{V_o}}^{\frac{K-a}{a}} \qquad \text{(B-10)}$$

Equation (B-10) shows that, as time progresses during the stripping operation, the concentration of methanol declines from its initial value of x_o. The quantity, a, in Equation (10) was computed from the experimental data by

$$a = [V_o - V_E]\ tQ \qquad \text{(B-11)}$$

where V_o and V_F were the initial and final liquid volumes in the basin (i.e., at 5 = o and t = t).

The important utility of Equation (B-11) was obtaining K from the experimental data. Taking the logarithm of both sides of the equation yielded

$$\log x = \log x_o/V_o + (K - a)/a \log [V_o - aQt] \ . \qquad \text{(B-12)}$$

It can be seen from this equation that a log-log plot of x versus $(1 - aQt/V_o)$ resulting in a straight line would have a slope of (K - a)/a from which K may be calculated.

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APPENDIX C

1983 WET MODEL WASTE DATA BASE

A summary of the waste characterization is provided in Table C-1. For each waste stream number used in the 1983 version of the WET Model Data Base (e.g. 01.01.03) the table provided a generic description of the waste stream (i.e. its "name"); the EPA number, where applicable; the Standard Industrial Code (SIC) for the generating industries; the generation rate; the number of generating facilities; and the "constituents of concern" contained in the waste (i.e. Appendix VIII compounds or compounds which make the waste ignitable, reactive, corrosive or EP toxic).

This table is adapted from Exhibit 2-3 of "W-E-T Model Hazardous Waste Data Bases, Second Draft," prepared by SCS Engineers of the Office of Solid Waste, U.S. EPA, July 21, 1983.

Note that the WET Model Data Base has since been expanded and revised, and its waste identifier numbers have been changed. Table C-1 is provided to identify waste streams listed in Table 6-1 of the current report. In many cases, data in Table C-1 is not quantitatively representative of more recent versions of the WET Model Data Base. However, the data does provide qualitative information of the waste streams analyzed in Section 6. The reader is referred to the above 1983 reference for detailed stream composition.

TABLE C-1. SUMMARY OF 1983 WET MODEL DATA BASE WASTE STREAM CHARACTERISTICS

WASTE STREAM NUMBER/NAME	EPA NO.	SIC NO.	1000 TONS /YEAR	NO. OF FACILITIES	CONSTITUENTS OF CONCERN
01. AQUEOUS INORGANICS					
01 01. METAL SLUDGES					
01.01.01 LEAD SLUDGES FROM CHLORALKALI PRODUCTION BY THE DIAPHRAGM CELL PROCESS		2812	25.90	6	LEAD
01.01.02 BRINE PURIFICATION MUDS FROM THE MERCURY CELL PROCESS IN CHLORINE PRODUCTIO	K071	2812	39.00	13	MERCURY
01.01.03 WASTEWATER TREATMENT SLUDGE FROM THE MERCURY CELL PROCESS IN CHLORINE PRODU	K106	2812	7.00	26	MERCURY
01.01.04 COOLING TOWER SLUDGE FROM THE PETROLEUM REFINING INDUSTRY.		2911	20.60	225	CHROMIUM (VI) LEAD
01.01.05 WASTEWATER TRMT SLUDGE FROM TITANIUM DIOXIDE PROD BY CHLORIDE PROCESS		2816	742.10	8	CHROMIUM (VI)
01.01.06 WASTEWATER TREATMENT SLUDGES FROM THE PRODUCTION OF CHROME PIGMENTS	K002 K003	2816	27.00	11	CHROMIUM (VI) LEAD
01.01.07 WASTEWATER TREATMENT SLUDGE FROM WOOD PRESERVING USING CHROMATED COPPER ARS		2491	25.10	120	ARSENIC COPPER CHROMIUM (VI)
01.01.08 SURFACE IMPOUNDMENT DREDGED SOLIDS FROM PRIMARY LEAD SMELTING FACILITIES	K065	3332	42.00	4	CADMIUM LEAD
01.01.09 TREATMT PROCESS WASTEWATER SLUDGES & ACID PLANT BLOWDOWN FROM ZINC PRODUCTI	K066	3333	11.00	68	CADMIUM LEAD
01.01.10 ELECTROLYTIC ANODE SLEEVES AND SLUDGES FROM PRIMARY ZINC PRODUCTION	K067	3333	16.00	5	CADMIUM LEAD
01.01.11 LEAD SLUDGES FROM BATTERY PRODUCTION		3691	150.00	202	LEAD
01.01.12 MIXED METAL SLUDGES FROM PAINT PRODUCTION		2851	30.00	1489	LEAD MERCURY THALLIUM

(Continued)

TABLE C-1. SUMMARY OF 1983 WET MODEL DATA BASE WASTE STREAM CHARACTERISTICS (CONTINUED)

WASTE STREAM NUMBER/NAME	EPA NO.	SIC NO.	1000 TONS /YEAR	NO. OF FACILITIES	CONSTITUENTS OF CONCERN
01.01.13 MIXED METAL SLUDGES FROM INK FORMULATION	K086	2893	10.00	453	CHROMIUM (VI) LEAD
01.01.14 ACID PLANT BLOWDOWN SLURRY SLUDGE FROM PRIMARY COPPER PRODUCTION	K064	3331	640.00	17	CADMIUM LEAD
01.01.15 CADMIUM PLANT LEACHATE RESIDUE FROM PRIMARY ZINC PRODUCTION	K068	3333	.50	5	CADMIUM LEAD
01.01.16 WASTEWATER TREATMENT SLUDGES FROM ELECTROPLATING OPERATIONS	F006 F008	3471 3479	488.40	4522	COPPER CHROMIUM (VI) CADMIUM LEAD NICKEL
01.01.17 WASTEWATER TREATMENT SLUDGES FROM THE MANUFACTURING AND PROCESSING OF EXPLO	K044	2892	1.70	29	LEAD
01.01.18 EMISSION CONTROL SLUDGE FROM SECONDARY LEAD SMELTING	K069	3341	28.60	3	CADMIUM CHROMIUM (VI) LEAD
01.01.19 WASTEH20 TRTMT SLUDGES FROM PROCESS & METAL FINISHING SOLNS FROM CU FORMING		3351	8.00	20	COPPER
01.01.20 ZINC SLUDGES FROM TEXTILES INDUSTRY		2823	160.00	24	ZINC
01.02. SOLUTIONS CONTAINING HEAVY METALS					
01.02.01 SPENT PICLKE LIQUOR FROM STEEL FINISHING OPERATIONS	K062	3312	2950.00	689	CHROMIUM (VI) LEAD
01.02.02 SPENT CLEANING AND ELECTROPLATING PROCESS SOLUTIONS	F007 F009	3471 3479	1990.00	4522	CADMIUM COPPER CYANIDE CHROMIUM (VI) NICKEL

(Continued)

TABLE C-1. SUMMARY OF 1983 WET MODEL DATA BASE WASTE STREAM CHARACTERISTICS (Continued)

WASTE STREAM NUMBER/NAME	EPA NO.	SIC NO.	1000 TONS /YEAR	NO. OF FACILITIES	CONSTITUENTS OF CONCERN
01.02.03 UNTREATED WASTEWATER FROM MANUFACTURE OF EXPLOSIVES		2892	24000.00	48	LEAD
01.02.04 SPENT ELECTROLESS NICKEL PLATING PROCESS SOLUTIONS		3471 3479	30.70	3090	COPPER CYANIDE FLUORINE (FLUORIDES NICKEL
01.02.05 UNTREATED RINSE WATER FROM ELECTROPLATING		3471 3479	17.30	4522	COPPER CYANIDE CHROMIUM (VI) NICKEL FLUORINE (FLUORIDES ZINC
01.03. CYANIDE SLUDGE					
01.03.01 AMMONIA STILL LIME SLUDGE FROM COKING OPERATIONS	K060	3312	72.00	62	CYANIDE PHENOL ARSENIC
01.03.02 HEAT TREATMENT WASTES	F010	3398	6.00	95	CYANIDE
01.04. BIOSLUDGES CONTAINING HEAVY METALS					
01.04.01 WASTE BIO SLUDGE FROM THE PETROLEUM REFINING INDUSTRY		2911	263.90	140	CHROMIUM (VI) LEAD
01.04.02 WASTEWATER TREATMENT SLUDGE FROM PRODUCTION OF ROSIN-BASED DERIVATIVES		2861	28.40	13	CHROMIUM (VI) ZINC

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TABLE C-1. SUMMARY OF 1983 WET MODEL DATA BASE WASTE STREAM CHARACTERISTICS (Continued)

WASTE STREAM NUMBER/NAME	EPA NO.	SIC NO.	1000 TONS /YEAR	NO. OF FACILITIES	CONSTITUENTS OF CONCERN
01.04.03 WASTEWATER TREATMENT SLUDGE FROM PRODUCTION OF SULFATE TURPENTINE (CR, CU,		2861	11.50	7	CHROMIUM (VI) COPPER NICKEL
01.04.04 WASTEWATER TRTMT SLUDGE FROM PROD OF GUM & WOOD CHEM EXC ROSIN-BASED AND SU		2861	96.20	33	CHROMIUM (VI)
01.05. OTHER AQUEOUS INORGANICS					
01.05.01 ASBESTOS SEPARATOR WASTES FROM DIAPHRAGM CELL PROCESS IN CHLORINE PRODUCTIO		2812	3.80	40	ASBESTOS
01.05.02 ARSENIC SLUDGE FROM PRODUCTION OF VETERINARY PHARMACEUTICALS	K084	2833	.50	3	ARSENIC
02. AQUEOUS ORGANICS					
02.01. PHENOLS					
02.01.01 WASTEWATER TRTMT SLUDGE FROM WOOD PRESERVING PROCESSES USING PENTACHLOROPHE	K001	2491	15.40	74	PENTACHLOROPHENOL
02.01.02 PHENOLIC SLUDGE FROM PLASTICS PRODUCTION		2821	53.00	816	PHENOL
02.01.03 PHENOL-FORMALDEHYDE SOLUTION FROM PLASTICS PRODUCTION		2821	486.00	816	PHENOL FORMALDEHYDE
02.02. WASTEWATER FR ORGANIC CHEM PRODUCT					
02.02.01 DISTILLATION BOTTOMS FROM ACETALDEHYDE PRODUCTION FROM ETHYLENE OXIDATI	K009	2869	399.50	3	CHLOROFORM FORMALDEHYDE
02.02.02 BOTTOM STREAMS FROM THE PRODUCTION OF K011, K013, AND K014	K011 K013 K014	2869	3181.00	6	ACRYLONITRILE CYANIDE ACETONITRILE
02.02.03 SPENT CATALYST OR CATALYST PURGE FROM FLUOROCARBON PRODUCTION	K021	2869	.27	2	ANTIMONY CARBON TETRACHLORID CHLOROFORM

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TABLE C-1. SUMMARY OF 1983 WET MODEL DATA BASE WASTE STREAM CHARACTERISTICS (Continued)

WASTE STREAM NUMBER/NAME	EPA NO.	SIC NO.	1000 TONS /YEAR	NO. OF FACILITIES	CONSTITUENTS OF CONCERN
02.02.04 WASTEWATER FROM ANILINE PRODUCTION FROM NITROBENZENE HYDROGENATION	K103	2865	39.95	8	NITROBENZENE BENZENE ANILINE
02.02.05 PROCESS WASTEWATER FROM CHLOROBENZENE PRODUCTION BY BENZENE CHLORINATIO	K105	2865	.52	7	BENZENE CHLOROBENZENE 1,2-DICHLOROBENZENE 1,4-DICHLOROBENZENE
02.02.06 STRIP STILL TAILS FROM METHYL ETHYL PYRIDINE PROD FROM PARALDEHYDE	K026	2869	1.44	1	PARALDEHYDE PYRIDINE 2-PICCOLINE
02.02.07 LIGHT ENDS FROM GLYCERIN PRODUCTION FROM ALLYL CHLORIDE		2869	2.10	2	TOLUENE
02.02.08 VENT SCRUBBER EFFLUENT FROM MALEIC ANHYDRIDE PROD BY BENZENE OXIDATION		2865	90.80	8	BENZENE MALEIC ANHYDRIDE
02.02.09 WASTEWATER FROM ETHYLENE DICHLORIDE PROD BY COMBINED PROCESS/ ETHYLENE		2869	172.50	20	1,2-DICHLOROETHANE VINYL CHLORIDE METHYL CHLORIDE CHLOROFORM CARBON TETRACHLORID
02.02.10 SPRAY SCRUBBER EFFLUENT FROM PHTHALIC ANHYDRIDE BY NAPHTHALENE PROCESS		2865	30.00	11	MALEIC ANHYDRIDE PHTHALIC ANHYDRIDE

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TABLE C-1. SUMMARY OF 1983 WET MODEL DATA BASE WASTE STREAM CHARACTERISTICS (Contiunued)

WASTE STREAM NUMBER/NAME	EPA NO.	SIC NO.	1000 TONS /YEAR	NO. OF FACILITIES	CONSTITUENTS OF CONCERN
02.02.11 AMINE RECOVERY FROM METHYLENE DIPHENYL DIICOSYANATE PROD BY ANILINE CON		2865	187.00	4	ANILINE
02.02.12 HEAVY ENDS FROM ETHYLENE OXIDE PRODUCTION FROM ETHYLENE OXIDATION		2869	15.50	15	ACETALDEHYDE
02.02.13 QUENCH BLOWDOWN FROM ETHYLENE PROD BY THERMAL CRACKING OF NATURAL GAS		2869	8172.00	35	TOLUENE PHENOL BENZENE
02.02.14 QUENCH BLOWDOWN FROM ETHYLENE PROD BY THERMAL CRACKING OF HEAVY LIQUIDS		2869	5448.00	35	TOLUENE PHENOL BENZENE
02.02.15 QUENCH TOWER WASTES FROM METHYL METHACRYLATE PROD BY ACETONE CYANOHYDRI		2869	1398.30	4	METHYL METHACRYLATE
02.02.16 DECANTER WASTES FROM PHENOL PROD BY CUMENE HYDROPEROXIDE CLEAVAGE		2865	1398.00	12	PHENOL
02.02.17 COOLING TOWER LOSSES FROM PROD OF ETHYLENE OXIDE BY OXID OF ETHYLENE		2869	291.50	15	ETHYLENE OXIDE
02.02.18 COMBINED WASTEWATER FROM DIMETHYL TEREPHTHALATE P-XYLENE OXID & ESTERIF		2865	136.20	5	FORMALDEHYDE
02.02.19 COMBINED WASTEWATER FROM PROD OF BISPHENOL-A BY ACETONE/PHENOL PROCESS		2865	118.00	5	PHENOL
02.02.20 CAUSTIC SCRUBBER EFF FROM PERCHLOROETHYLENE & CARBON TET PROD BY CHLOR		2869	45.40	10	CARBON TETRACHLORID
02.02.21 ACETOPHENONE COLUMN SEPARATOR FROM PHENOL PROD BY CUMENE HYDROPEROXIDE		2865	12.50	12	PHENOL
02.02.22 WASTEWATER/DEHYDRATION FROM METHYL ETHYL KETONE PROD BY S-BUTANOL DEHYD		2869	3.63	6	METHYL ETHYL KETONE
02.02.23 AZEOTROPE DECANTER EFF FROM GLYCERIN PROD BY HYDROGENATION OF ACROLEIN		2869	2.72	1	METHYL ETHYL KETONE
02.03. WWTP SLUDGE FR PESTICIDE PRODUCT					
02.03.01 TOXAPHENE WASTE	K041	2879	5.00	2	TOXAPHENE
02.03.90 PESTICIDE WASTES - HIGH TOXICITY, N.O.S.		2879	500.00	439	PARATHION
02.03.91 PESTICIDE WASTES - MODERATE TOXICITY, N.O.S.					

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TABLE C-1. SUMMARY OF 1983 WET MODEL DATA BASE WASTE STREAM CHARACTERISTICS (Continued)

WASTE STREAM NUMBER/NAME	EPA NO.	SIC NO.	1000 TONS /YEAR	NO. OF FACILITIES	CONSTITUENTS OF CONCERN
02.04. OTHER AQUEOUS ORGANICS					
02.04.01 WASTEWATER TRTMT SLUDGE FROM WOOD PRESERVING PROCESSES THAT USE CREOSOTE	K001	2491	35.70	171	ACENAPHTHENE CHRYSENE FLUORENE
03. CONCENTRATED ORGANICS					
03.01. SPENT SOLVENTS					
03.01.01 TRICHLOROETHYLENE SPENT SOLVENT WASTE	F001		18.00	3150	TRICHLOROETHYLENE
03.01.02 1,1,1-TRICHLOROETHANE SPENT SOLVENT WASTE	F001		16.00	8330	1,1,1-TRICHLOROETHA
03.01.03 METHYLENE CHLORIDE SPENT SOLVENT WASTE	F001		3.00	4776	DICHLOROMETHANE
03.01.04 TETRACHLOROETHYLENE SPENT SOLVENT WASTE	F002	721	67.00	8000	TETRACHLOROETHENE
03.01.05 SPENT DEGREASING SOLVENTS FROM METAL CLEANING OPERATIONS FOR ELECTROPLATING	F001	3471 3479	18.00	1085	1,1,2,2-TETRACHLORO TRICHLOROETHYLENE DICHLOROMETHANE 1,1,1-TRICHLOROETHA HEXANE TOLUENE
03.01.06 DEGREASER SLUDGE FROM METAL CLEANING OPERATIONS FOR ELECTROPLATING OPERATIO	F001	3471 3479	14.20	1085	1,1,1-TRICHLOROETHA TRICHLOROETHYLENE
03.01.90 SPENT SOLVENTS N.O.S.	F004		15.00	2055	TOLUENE
03.02. STILL BOTTOMS FR SOLVENT RECOVERY					
03.02.01 TRICHLOROETHYLENE STILL BOTTOMS	F001		18.00	3150	TRICHLOROETHYLENE
03.02.02 1,1,1-TRICHLOROETHANE STILL BOTTOMS	F001		15.00	960	1,1,1-TRICHLOROETHA
03.02.03 METHYLENE CHLORIDE STILL BOTTOMS	F001		2.00	6493	DICHLOROMETHANE

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EPA Form 2350-4 (4-80)
(PREVIOUSLY CIN. EPA FORM 287)

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TABLE C-1. SUMMARY OF 1983 WET MODEL DATA BASE WASTE STREAM CHARACTERISTICS (Continued)

WASTE STREAM NUMBER/NAME	EPA NO.	SIC NO.	1000 TONS /YEAR	NO. OF FACILITIES	CONSTITUENTS OF CONCERN
03.02.90 STILL BOTTOMS N.O.S.	F004		15.00	2055	TOLUENE
03.03. SOLVENT/METAL SLUDGES					
03.03.01 PAINT APPLICATION SLUDGES			29.00	2220	TOLUENE METHYL ETHYL KETONE CHROMIUM (VI) LEAD MERCURY
03.03.90 ORGANIC / METALLIC SLUDGES N.O.S.			73.00	396	CHROMIUM (VI)
03.04. LIQ RESIDUES FR ORG CHEM PRODUCT					
03.04.01 STILL BOTTOMS FROM BENZYL CHLORIDE PROD BY PHOTOCHLORINATION OF TOLUENE	K015	2865	8.38	1	1,2,4-TRICHLOROBENZ HEXACHLOROBENZENE TOLUENE
03.04.02 HEAVY ENDS FROM EPICHLOROHYDRIN PRODUCTION FROM ALLYL CHLORIDE	K017	2869	6.36	3	EPICHLOROHYDRIN 1,2-DICHLOROPROPANE
03.04.03 FRACTIONATING COLUMN BOTTOMS FROM ETHYL CHLORIDE PROD BY ETHYLENE HYDRO	K018	2869	35.40	5	1,2-DICHLOROETHANE HEXACHLOROBENZENE HEXACHLOROBUTADIENE TRICHLOROETHYLENE
03.04.04 HEAVY ENDS FROM DISTILLATION FROM ETHYLENE DICHLORIDE PROD BY COMBINED	K019	2869	80.30	17	1,2-DICHLOROETHANE 1,1,3-TRICHLOROETHA 1,1,1,2-TETRACHLOROE 1,1,2,2-TETRACHLORO

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TABLE C-1. SUMMARY OF 1983 WET MODEL DATA BASE WASTE STREAM CHARACTERISTICS (Continued)

WASTE STREAM NUMBER/NAME	EPA NO.	SIC NO.	1000 TONS /YEAR	NO. OF FACILITIES	CONSTITUENTS OF CONCERN
03.04.05 HEAVY ENDS FROM VINYL CHLORIDE PROD BY DEHYDROCHLOR OF ETHYLENE DICHLOR	K020	2869	52.70	15	VINYL CHLORIDE 1,1,1,2-TETRACHLOROE 1,1,2-TRICHLOROETHAN 1,2-DICHLOROETHANE
03.04.06 LIGHT ENDS FROM PHTHALIC ANHYDRIDE PRODUCTION FROM NAPHTHALENE	K023	2865	.76	11	PHTHALIC ANHYDRIDE MALEIC ANHYDRIDE
03.04.07 LIGHT ENDS FROM PHTHALIC ANHYDRIDE PRODUCTION BY O-XYLENE PROCESS	K093	2865	2.10	11	PHTHALIC ANHYDRIDE MALEIC ANHYDRIDE
03.04.08 LIQUID ORGANICS FROM HEXAMETHYLENE DIAMINE PROD BY 1,6-HEXANEDIOL AMMON		2869	5.80	1	CYCLOHEXANE
03.04.09 DISTILLATION BOTTOMS FROM NOITROBENZENE PROD BY NITRATION OF BENZENE	K025	2865	1.50	7	M-DINITROBENZENE NITROBENZENE 4-NITROPHENOL 2,4-DINITROTOLUENE
03.04.10 CARBON TET REMOVAL EFF FROM PERCHLOROETHYLENE PROD BY OXYCHLORINATION		2869	.96	9	CARBON TETRACHLORID TRICHLOROETHYLENE
03.04.11 HEAVY ENDS FROM PROD OF TRICHLOROETHYLENE AND PERCHLOROETHYLENE	K030	2869	48.40	10	HEXACHLOROBENZENE HEXACHLOROBUTADIENE 1,1,2,2-TETRACHLORO 1,1,1,2-TETRACHLOROE
03.04.12 STILL BOTTOMS FROM PROD OF CHLOROBENZENES BY CHLORINATION OF BENZENE	K085	2865	4.50	7	HEXACHLOROBENZENE

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TABLE C-1. SUMMARY OF 1983 WET MODEL DATA BASE WASTE STREAM CHARACTERISTICS (Continued)

WASTE STREAM NUMBER/NAME	EPA NO.	SIC NO.	1000 TONS /YEAR	NO. OF FACILITIES	CONSTITUENTS OF CONCERN
03.04.13 DISTILLATION BOTTOM TARS FROM PHENOL PROD BY CUMENE HEDROPEROXIDE CLEAV	K022	2865	106.20	12	BENZO(A)ANTHRACENE BENZO(A)PYRENE CHRYSENE PHENOL
03.04.14 DISTILLATION SIDE CUT FROM ACETALDEHYDE PROD BY ETHYLENE OXIDATION	K010	2869	26.30	3	ACETALDEHYDE CHLOROACETALDEHYDE CHLOROFORM FORMALDEHYDE
03.04.15 STILL BOTTOMS FROM ANILINE PRODUCTION FROM NITROBENZENE HYDROGENATION	K083	2865	1.80	9	DIPHENYLAMINE PHENYLENEDIAMINE NITROBENZENE BENZENE ANILINE
03.04.16 STEAM STRIPPER WASTE FROM 1,1,1-TRICHLOROETHANE PROD BY HYDROCHLORINATI	K029	2869	1.30	3	1,2-DICHLOROETHANE 1,1,1-TRICHLOROETHA
03.04.17 HEAVY RESIDUES FROM MALEIC ANHYDRIDE PRODUCTION BY BENZENE OXIDATION		2869	3.60	8	MALEIC ANHYDRIDE
03.04.18 HEAVY ENDS FROM CYCLOHEXANOL PRODUCTION BY PHENOL HYDROGENATION		2865	5.60	7	PHENOL
03.04.19 LIGHT ENDS FROM CYCLOHEXANOL PRODUCTION FROM PHENOL HYDROGENATION		2869	2.70	7	BENZENE CYCLOHEXANE
03.04.20 WASTE SOLVENTS FROM CYANURIC CHLORIDE PROD BY HYDROGEN CYANIDE CHLORINA		2865	17.30	4	CARBON TETRACHLORID TOLUENE

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TABLE C-1. SUMMARY OF 1983 WET MODEL DATA BASE WASTE STREAM CHARACTERISTICS (Continued)

WASTE STREAM NUMBER/NAME	EPA NO.	SIC NO.	1000 TONS /YEAR	NO. OF FACILITIES	CONSTITUENTS OF CONCERN
03.04.21 RESIDUE FROM BENZENE PRODUCTION BY TOLUENE HYDRODEALKYLATION		2865	22.70	53	TOLUENE BENZENE
03.04.22 CO-PRODUCT WASTE FROM ACETIC ACID PROD BY N-BUTANE OXIDATION		2869	101.70	11	METHYL ETHYL KETONE
03.04.23 HEAVY ENDS FROM ALLYL CHLORIDE PROD BY PROPYLENE CHLORINATION		2869	8.20	3	1,3-DICHLOROPROPENE
03.04.24 LIGHT ENDS FROM S-BUTYL ALCLHOL PROD BY HYDROLYSIS OF BUTYLENES		2869	22.70	4	METHYL ETHYL KETONE
03.04.25 FINISHING COLUMN HEAVY ENDS FROM ACRYLIC ACID PROD BY MODIFIED REPPE		2869	2.60	1	COPPER NICKEL
03.04.26 ACETALDEHYDE COLUMN WASTE FROM ACROLEIN PROD BY PROPYLENE OXIDATION		2869	1.40	1	ACETALDEHYDE ACROLEIN
03.04.27 WASTE ALCOHOLS FROM 1,1-DIMETHYLHYDRAZINE PROD BY DIMETHYLAMINE PROCESS		2869	4.50	1	FORMALDEHYDE
03.04.28 ALLYL ALCOHOL RECOVERY WASTE FROM GLYCERIN PROD BY HYDROGEN OF ACROLEIN		2869	1.40	2	ACROLEIN 1,1-DICHLOROETHENE
03.04.29 HEAVY ENDS FROM GLYCERIN PURIFICATION FROM GLYCERIN PROD BY HYDROGEN OF		2869	.82	2	2-CHLOROPHENOL
03.04.30 HEAVY ENDS-ALLYL ALCOHOL RECOVERY FROM GYLCERIN PROD BY HYDROGEN OF ACR		2869	1.60	1	ACROLEIN METHYL ETHYL KETONE ALLYL ALCOHOL
03.04.31 STILL BOTTOMS FROM BEXZYL CHLORIDE PROD BY CATALYTIC CHLORIN OF TOLUENE	K015	2865	.68	2	BENZOTRICHLORIDE 1,2,4-TRICHLOROBENZ HEXACHLOROBENZENE TOLUENE

(Contiunued)

TABLE C-1. SUMMARY OF 1983 WET MODEL DATA BASE WASTE STREAM CHARACTERISTICS (Continued)

WASTE STREAM NUMBER/NAME	EPA NO.	SIC NO.	1000 TONS /YEAR	NO. OF FACILITIES	CONSTITUENTS OF CONCERN
03.04.32 PRODUCTION WASTES FROM QUATERNARY AMINE (DISINFECTANTS) MANUFACTURE		2869	.04	20	TOXAPHENE DIMETHYL ALKYLAMINE
03.05. SOLID RESIDUES FR ORG CHEM PRODUCT					
03.05.01 HEAVY ENDS FROM CARBON TETRACHLORIDE PROD BY METHANE CHLORINATION	K016	2869	1.60	10	HEXACHLOROBENZENE HEXACHLOROBUTADIENE HEXACHLOROETHANE TETRACHLOROETHENE
03.05.02 HEAVY BOTTOMS FROM PHTHALIC ANHYDRIDE PRODUCTION FROM O-XYLENE	K016	2865	.70	11	PHTHALIC ANHYDRIDE
03.05.03 DISTILLATION BOTTOMS FROM 1,1,1-TRICHLOROETHANE PROD BY HYDROCHLORINATI	K095	2869	35.50	4	1,1,1,2-TETRACHLOROE 1,1,2,2-TETRACHLORO
03.05.04 HEAVY ENDS FROM 1,1,1-TRICHLOROETHANE PROD BY ETHANE CHLORINATION	K096	2869	3.20	1	1,2-DICHLOROETHANE 1,1,1-TRICHLOROETHA 1,1,2-TRICHLOROETHAN 1,1,1,2-TETRACHLOROE 1,1,2,2-TETRACHLORO HEXACHLOROETHANE
03.05.05 CENTRIFUGE & DISTILLATION RESIDUES FROM TOLUENE DIISOCYNATE PRODUCTION	K027	2865	107.90	8	TOLUENE DIAMINE TOLUENE DIISOCYANAT
03.05.06 DISTILLATION BOTTOMS FROM PHTHALIC ANHYDRIDE PROD FROM NAPHTHALENE	K024	2865	2.50	11	PHTHALIC ANHYDRIDE TRICHLOROETHYLENE
03.03.07 FOOTS FROM FILM EVAPORATOR FROM GLYCERIN PRODUCTION FROM ALLYL CHLORIDE		2869	9.10	2	DICHLOROPROPANOLS TRICHLOROPROPANE SODIUM

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(PREVIOUSLY CIN. EPA FORM 287)
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TABLE C-1. SUMMARY OF 1983 WET MODEL DATA BASE WASTE STREAM CHARACTERISTICS (Continued)

WASTE STREAM NUMBER/NAME	EPA NO.	SIC NO.	1000 TONS /YEAR	NO. OF FACILITIES	CONSTITUENTS OF CONCERN
03.05.08 SPENT CATALYST FROM 1,1,1-TRICHLOROETHANE PROD BY VINYL CHLORIDE PROCES	K028	2869	.61	4	1,1,3-TRICHLOROETHA ACETYL CHLORIDE 1,1,2,2-TETRACHLORO PENTACHLOROETHANE
03.05.09 DISTILLATION BOTTOMS FROM LINEAR ALKYL BENZENE SULFONATE PRODUCTION		2869	43.65	48	NAPHTHALENE
03.06. OTHER CONCENTRATED ORGANICS					
03.06.01 CHLORINATED HYDROCARBON WASTE FROM THE PURIFICATION STEP OF THE DIAPHRAGM C	K073	2812	.34	6	CHLOROFORM CARBON TETRACHLORID
03.06.02 DECANTER TANK TAR SLUDGE FROM COKING OPERATIONS	K087	3312	39.80	36	NAPHTHALENE PHENOL
03.06.03 PCB FLUIDS			4.50	6163	PCB-1254 1,2,4-TRICHLOROBENZ
04. OILY WASTES					
04.01. OILY WASTES FR PETROLEUM REFINING					
04.01.01 DISSOLVED AIR FLOATATION (DAF) FLOAT FROM THE PETROLEUM REFINING INDUSTRY	K048	2911	297.60	160	CHROMIUM (VI) LEAD
04.01.02 SLOP OIL EMULSION SOLIDS FROM THE PETROLEUM REFINING INDUSTRY	K049	2911	92.40	171	CHROMIUM (VI) LEAD
04.01.03 HEAT EXCHANGER BUNDLE CLEANING SLUDGE FROM THE PETROLEUM REFINING INDUSTRY	K050	2911	1.70	106	CHROMIUM (VI) LEAD
04.01.04 API SEPARATOR SLUDGE FROM THE PETROLEUM REFINING INDUSTRY	K051	2911	196.20	205	CHROMIUM (VI) LEAD

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EPA Form 2350-4 (4-80)
(PREVIOUSLY CIN: EPA FORM 287)
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TABLE C-1. SUMMARY OF 1983 WET MODEL DATA BASE WASTE STREAM CHARACTERISTICS (Continued)

WASTE STREAM NUMBER/NAME	EPA NO.	SIC NO.	1000 TONS /YEAR	NO. OF FACILITIES	CONSTITUENTS OF CONCERN
04.01.05 LEADED TANK BOTTOMS FROM THE PETROLEUM REFINING INDUSTRY	K052	2911	7.10	185	CHROMIUM (VI) LEAD
04.01.06 NON-LEADED TANK BOTTOMS FROM THE PETROLEUM REFINING INDUSTRY	----	2911	154.70	140	CHROMIUM (VI) LEAD
04.01.07 CRUDE TANK BOTTOMS FROM THE PETROLEUM REFINING INDUSTRY	----	2911	1.00	153	CHROMIUM (VI) LEAD
04.01.08 SILT FROM STORM WATER RUNOFF FROM THE PETROLEUM REFINING INDUSTRY	----	2911	40.30	140	CHROMIUM (VI) LEAD
04.02. OTHER OILY WASTES					
04.02.01 SPENT CLAY FROM OIL RE-REFINING		2992	69.00	6	LEAD BENZO(A)ANTHRACENE BENZO(A)PYRENE
04.02.02 ACID TAR FROM OIL RE-REFINING		2992	32.00	6	LEAD BENZO(A)ANTHRACENE BENZO(A)PYRENE
04.02.03 CAUSTIC SLUDGE FROM RE-REFINING		2992	9.00	2	LEAD BENZO(A)ANTHRACENE BENZO(A)PYRENE
05. INORGANIC SOLID RESIDUES					
05.01. RESIDUES FR METAL SMLTG & REFINING					
05.01.01 EMISSION CONTROL DUST FROM THE PRIMARY PRODUCTION OF STEEL IN ELECTRIC FURN	K061	3312	463.60	70	CADMIUM CHROMIUM (VI) LEAD

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TABLE C-1. SUMMARY OF 1983 WET MODEL DATA BASE WASTE STREAM CHARACTERISTICS (Continued)

WASTE STREAM NUMBER/NAME	EPA NO.	SIC NO.	1000 TONS /YEAR	NO. OF FACILITIES	CONSTITUENTS OF CONCERN
05.01.02 EMISSION CONTROL SLUDGE FROM THE PRIMARY PRODUCTION OF STEEL IN ELECTRIC FU	K061	3312	70.00	16	CADMIUM CHROMIUM (VI) LEAD
05.01.03 SLUDGE FROM TIN PLATING MILL OPERATIONS	----	3312	30.00	10	CHROMIUM (VI) LEAD
05.01.04 SLUDGE FROM GALVANIZING MILL OPERATIONS	----	3312	60.00	63	CHROMIUM (VI)
05.01.05 DUST AND SLUDGE FROM FERROMANGANESE FURNACES	----	3313	83.60	12	LEAD
05.01.06 DUST AND SLUDGE FORM SILICOMANGANESE ELECTRIC FURNACES	----	3313	75.20	13	LEAD
05.01.07 DUST AND SLUDGE FROM FERROCHROME ELECTRIC FURNACES	----	3313	85.40	15	CHROMIUM (VI) LEAD
05.01.08 SLUDGE FROM FERRONICKEL PRODUCTION	----	3313	32.80	5	NICKEL CHROMIUM (VI)
05.01.09 CUPOLA, ELECTRIC ARC OR INDUCTION FURNACE DUSTS/SLUDGES FROM IRON AND STEEL	----	332_	2139.10	2000	CADMIUM LEAD
05.01.10 WASTE SAND FROM IRON AND STEEL FOUNDRY OPERATIONS	----	332_	16915.10	2000	CADMIUM
05.01.11 EMISSION CONTROL DUST FROM SECONDARY LEAD SMELTING	K069	3341	10.00	73	CADMIUM CHROMIUM (VI) LEAD
05.01.12 BLAST FURNACE SLAG FROM SECONDARY COPPER SMELTING	----	3341	153.30	30	COPPER ZINC LEAD
05.02. OTHER INORGANIC SOLID RESIDUES					

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PAGE NUMBER
EPA Form 2350-4 (4-80)
(PREVIOUSLY CIN. EPA FORM 287)
TYPING GUIDE SHEET

TABLE C-1. SUMMARY OF 1983 WET MODEL DATA BASE WASTE STREAM CHARACTERISTICS (Continued)

WASTE STREAM NUMBER/NAME	EPA NO.	SIC NO.	1000 TONS /YEAR	NO. OF FACILITIES	CONSTITUENTS OF CONCERN
05.02.01 FGD SLUDGE FROM CONVENTIONAL COAL COMBUSTION			24400.00	70	ARSENIC BARIUM CADMIUM LEAD SELENIUM
05.02.02 SCRAP BATTERIES		3692	1.30	41	CADMIUM LEAD MERCURY
05.02.03 RESIDUES FROM THE RUBBER INDUSTRY		30	52.00	196	BARIUM LEAD NICKEL VANADIUM ZINC CHROMIUM (VI)
05.02.04 FLYASH FROM CONVENTIONAL COAL COMBUSTION			40240.00	480	ARSENIC BARIUM CHROMIUM (VI) LEAD

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